CANADIAN JOURNAL OF RESEARCH

VOLUME 15 JULY, 1937 NUMBER 7

CONTENTS

SEC. A.—PHYSICAL SCIENCES

Page

The Refractive Indices of Liquid Oxygen, Nitrogen, and Hydrogen—*H. E. Johns and J. O. Wilhelm* - - - - - 101

The Coefficient of Heat Transfer for Vertical Surfaces in Still Air—*R. Ruedy* - - - - - - - - - - - - - 109

SEC. B.—CHEMICAL SCIENCES

An Investigation of the Chlorination of Spruce Wood and of the Resulting Chlorolignin—*G. V. Jansen and J. W. Bain* - 279

Free Radicals in Organic Decomposition Reactions. I. The Thermal Decomposition of Mixtures of Methyl Ether and Deutero-acetone—*E. W. R. Steacie and W. A. Alexander* - - 295

The Occurrence of "Mottled Enamel" of Teeth in Alberta and Its Relation to the Fluorine Content of the Water Supply —*O. J. Walker and E. Y. Spencer* - - - - - - - - 305

NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

Publications and Subscriptions

The Canadian Journal of Research is issued monthly in four sections, as follows;

A. Physical Sciences
B. Chemical Sciences
C. Botanical Sciences
D. Zoological Sciences

For the present, Sections A and B are issued under a single cover, as also are Sections C and D, with separate pagination of the four sections, to permit separate binding, if desired.

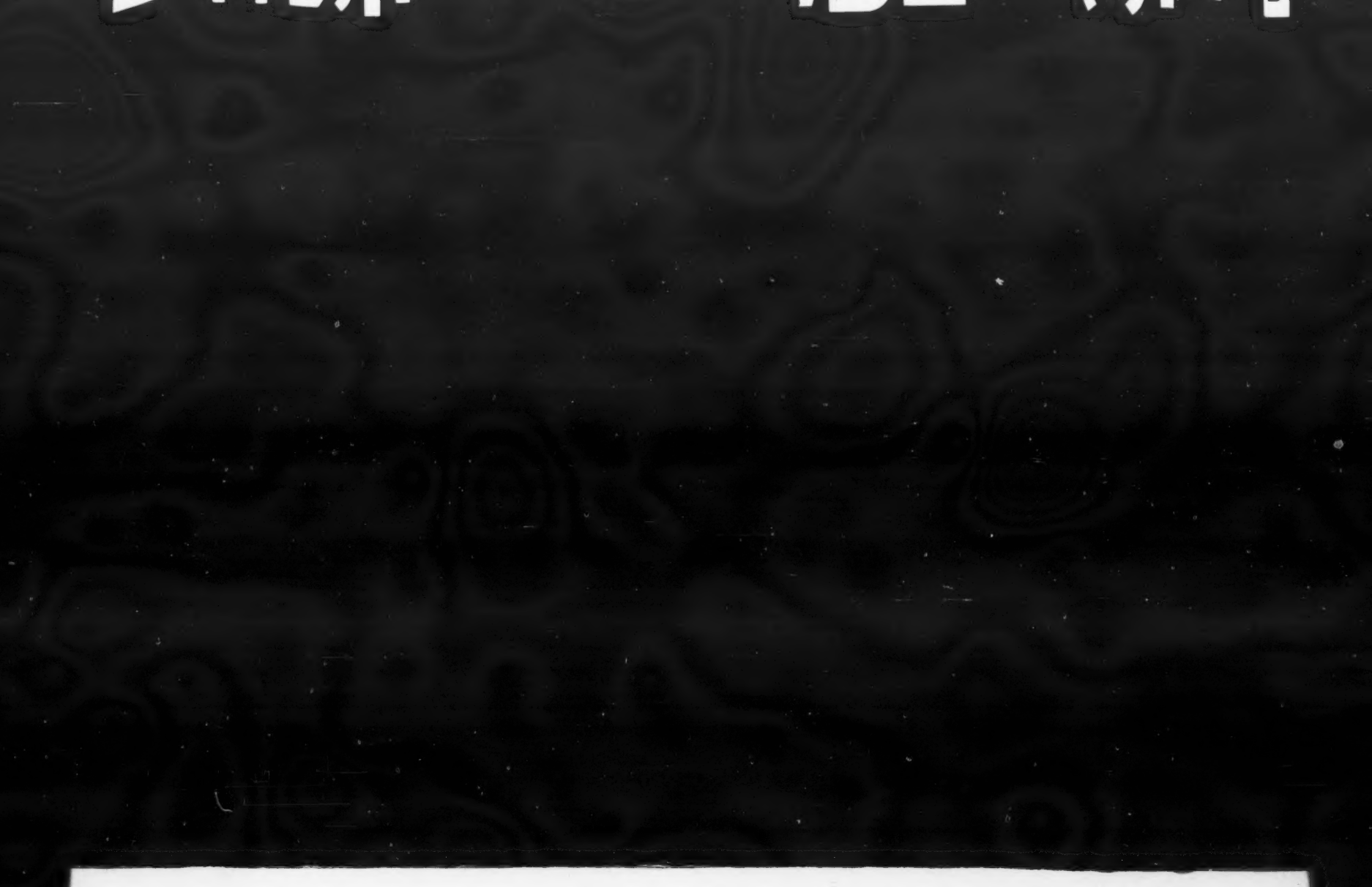
Subscription rates, postage paid to any part of the world (effective 1 April, 1939), are as follows:

	Annual	*Single Copy*
A and B	$ 2.50	$ 0.50
C and D	2.50	0.50
Four sections, complete	4.00	—

The Canadian Journal of Research is published by the National Research Council of Canada under authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. All correspondence should be addressed:

National Research Council, Ottawa, Canada.

Reprinted in entirety by photo-offset from the original issue.



Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 15, SEC. A. JULY, 1937 NUMBER 7

THE REFRACTIVE INDICES OF LIQUID OXYGEN, NITROGEN, AND HYDROGEN[1]

BY H. E. JOHNS[2] AND J. O. WILHELM[3]

Abstract

The refractive indices of liquid oxygen, nitrogen, and hydrogen at temperatures ranging from the normal boiling point to the normal freezing point of the liquefied gases were determined by means of a Wollaston cell for the wave-lengths 6939Å, 5461Å, and 4358Å. The values obtained at the normal boiling point for $\lambda = 5461$Å were: oxygen, 1.2242; nitrogen, 1.1990; hydrogen, 1.1120.

This research was undertaken with the purpose of measuring the refractive index of liquid helium I and II in an effort to throw additional light on the nature of helium II. As yet no final results have been obtained for helium, but in perfecting the apparatus new determinations have been made for oxygen, nitrogen, and hydrogen. Heretofore a complete set of data has not been available for these liquids, as only isolated measurements have been made in the past.

In 1891 Olszewski and Witrowski (8) found the refractive index of oxygen, at the normal boiling point, to be 1.2222 for the sodium D line. The following year Dewar and Liveing (3) obtained the value 1.226, and in 1893 worked out a dispersion curve, this time determining the index as 1.2214 (5). Dewar and Liveing (4) also made measurements on nitrogen at the normal boiling point and obtained the value 1.2053 for the index. In 1901 Dewar (2) found the value 1.12 for hydrogen by the apparent depth method.

In this research the refractive indices have been determined for three different wave-lengths at temperatures ranging from the normal boiling point to the normal freezing point of liquid oxygen, nitrogen, and hydrogen.

Experimental

An evacuated Wollaston cell was used by means of which the critical angle from the liquid to vacuum could be obtained, and hence the refractive index. The cell was constructed from two circular, plane polished pieces of Pyrex about 1 mm. thick and 3 cm. in diameter, sealed together around the edge by heating, leaving an air space of approximately 0.1μ. Through the skilful

[1] *Manuscript received April 17, 1937.*
Contribution from the McLennan Laboratory, Department of Physics, University of Toronto, Toronto, Canada.

[2] *Graduate student, University of Toronto, 1936-1937.*

[3] *Assistant Professor, Department of Physics, University of Toronto.*

efforts of Mr. R. H. Chappell a cell was produced that was practically free from distortion. The space between the two glass plates was then evacuated and the cell, *J*, mounted as shown in Fig. 1.

The liquid under consideration was placed in the flask *B* and light from a broad monochromatic source was passed through the flask and cell. The light was examined with a telescope focused for parallel light. When the cell was placed at the critical angle, the field of view of the telescope was divided into sharply defined bright and dark portions. Because the cell was so very thin, interference fringes were formed in the vacuum space, and were observed in the telescope when the cell was placed near the critical angle. In taking readings the cross hair was always set on the outermost fringe, which divided the bright and dark portions of the field of view.

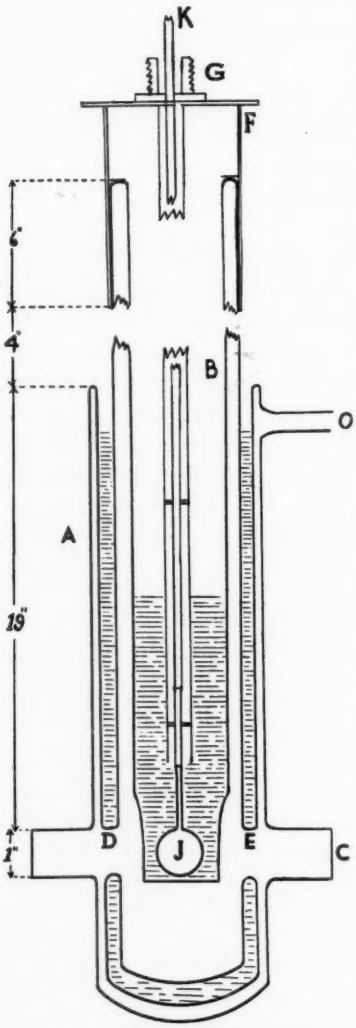


FIG. 1. *Diagram of apparatus.*

Fig. 1 shows the specially designed Pyrex flask, which consisted essentially of two vacuum flasks, *A* and *B*, so separated that liquid air might be kept between them to protect the liquid hydrogen or helium in the inner flask. The inside flask was made with parallel plane faces, and plane windows, *C*, were inserted in the outer flask. These flasks were joined at *D* and *E* in such a way that light did not have to pass through the liquid air. The common vacuum space surrounding *A* and *B* was maintained by a pump attached at *O*. The top of the flask was fitted with a German silver cover, *F*, into which was soldered the stuffing box, *G*. A $\frac{1}{2}$ in. German silver tube extending almost to *J* was attached to *G*. The cell was suspended from a $\frac{3}{16}$ in. German silver tube and this in turn from a brass rod, *K*, which could be turned in the stuffing box, *G*. By placing three circular guides in the outer German silver tube the long suspended rod could be rotated accurately about a vertical axis.

A divided circle with a fixed vernier was attached at *K* so that the angle

through which the cell was turned could be measured to the nearest minute. A flexible steel cable 5 ft. in length was connected to the slow motion screw so that the cell could be turned slowly to the critical position by an observer looking through the telescope at *C*. By turning the cell to four symmetrically placed positions, two values were obtained for each critical angle.

Difficulties were encountered in keeping the vernier from creeping slightly, as well as in making the cell rotate accurately about its vertical diameter. The apparatus had to be extremely rigid to prevent movement of the cell when the pressure in the inner flask was altered. In the measurements with the potassium red line, 6939 Å, it was difficult at times to obtain sufficient illumination and to keep out extraneous light. The most difficult problem, however, was to obtain a cell that was free from distortion. It was found that the measured critical angles differed on the two sides of the cell owing to the fact that the plates of glass were slightly prismatic, and that the measured angles varied slightly for different parts of the cell. The cell that was finally used gave two values which agreed to within three minutes. This cell was also checked with water. It gave the value 1.3346 as compared with the value 1.3342 as given in the International Critical Tables for water at 23° C. and light of wave-length 5461 Å. This difference corresponds to an error of one minute in the critical angle.

Results

The results obtained are given in Tables I, II, and III, and are represented graphically in Figs. 2 to 7. The values given in the tables are only those that were obtained under the best experimental conditions.

TABLE I

THE REFRACTIVE INDICES OF LIQUID OXYGEN BOILING AT DIFFERENT TEMPERATURES

Temp., ° K.	Density, gm. per cc.	Refractive index	$\frac{\mu^2-1}{\mu^2+2}$
λ=4358 Å			
90.3	1.1425	1.2277	0.1448
90.0	1.1435	1.2283	.1450
89.1	1.1485	1.2293	.1456
87.6	1.1555	1.2311	.1467
85.5	1.1655	1.2328	.1477
83.6	1.1747	1.2345	.1487
82.4	1.1805	1.2355	.1493
79.8	1.1931	1.2382	.1509
76.9	1.2070	1.2416	.1529
73.6	1.2228	1.2446	.1547
69.7	1.2415	1.2483	.1569
65.0	1.2640	1.2518	.1590
λ=5461 Å			
90.3	1.1425	1.2243	0.1426
90.0	1.1435	1.2241	.1425
89.1	1.1485	1.2251	.1431
87.6	1.1555	1.2271	.1443
86.5	1.1607	1.2276	.1446
85.6	1.1650	1.2295	.1457
85.4	1.1660	1.2293	.1456
λ=5461 Å—*Continued*			
83.7	1.1742	1.2308	0.1465
82.2	1.1815	1.2322	.1473
80.5	1.1898	1.2345	.1487
76.9	1.2070	1.2369	.1501
73.8	1.2218	1.2401	.1520
69.7	1.2415	1.2442	.1544
65.0	1.2640	1.2483	.1569
λ=6939 Å			
90.3	1.1425	1.2226	0.1416
90.0	1.1435	1.2233	.1420
87.5	1.1560	1.2258	.1435
87.3	1.1570	1.2262	.1437
87.1	1.1577	1.2263	.1438
83.7	1.1742	1.2293	.1453
79.8	1.1931	1.2330	.1478
77.0	1.2063	1.2347	.1488
73.8	1.2218	1.2382	.1509
69.7	1.2415	1.2417	.1530
65.7	1.2609	1.2441	.1544

Oxygen

The results for oxygen are given in Table I and are shown graphically in Figs. 2 and 3. Points marked by circles and dotted circles refer to readings taken during two separate experiments. Fig. 3 shows μ^2-1/μ^2+2 plotted against the density which was obtained by Mathias and Onnes (6), and Baly and Donnan (1).

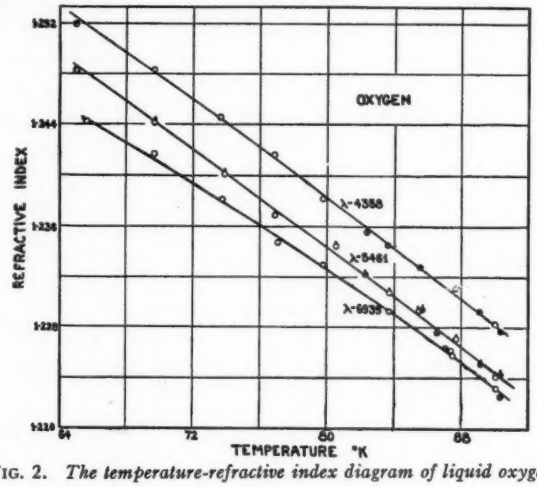


FIG. 2. *The temperature-refractive index diagram of liquid oxygen.*

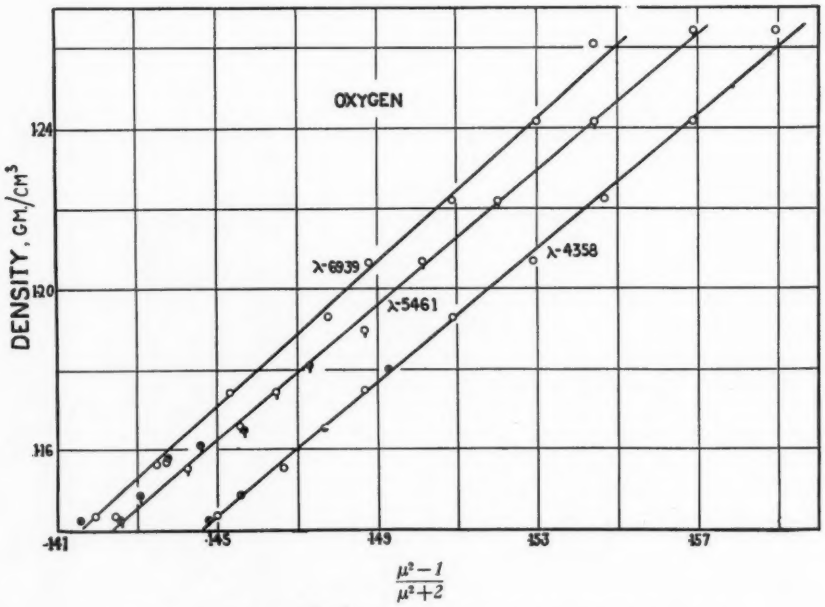


FIG. 3. *The function* $\frac{\mu^2-1}{\mu^2+2}$ *plotted against the density for liquid oxygen.*

The best values for the refractive indices of oxygen, at the normal boiling point 90.21° K., obtained from the graphs are: $\lambda = 4358$ Å, 1.2280; $\lambda = 5461$ Å, 1.2242; $\lambda = 6939$ Å, 1.2230.

An error of two minutes in the critical angle would introduce an error of ± 0.0005 in the value of the refractive index. As can be seen from the graph, few of the points deviate by more than this amount from the lines. It is possible that an error due to the interference fringes might have been introduced, for if the critical angle happened to come at a position of interference no line would be present to set on, and the second fringe would have been used. However, in all cases the cross hair was set on the outermost fringe even if it was faint. An error of $\frac{1}{4}$ fringe width introduces an error in the refractive index of 0.0002 for 4358 Å, 0.0003 for 5461 Å, and 0.0004 for 6939 Å. It is therefore likely that the errors in the present determinations are less than ± 0.0005. These values are higher than those of Dewar and Liveing, who obtained the value 1.2214 for the sodium D line (5). This difference corresponds to an error of 10 min. in the critical angle.

Nitrogen

The results obtained for nitrogen are given in Table II and are presented graphically in Figs. 4 and 5.

TABLE II

THE REFRACTIVE INDICES OF LIQUID NITROGEN BOILING AT DIFFERENT TEMPERATURES

Temp., ° K.	Density (7), gm. per cc.	Refractive index	$\frac{\mu^2-1}{\mu^2+2}$
$\lambda = 4358$ Å			
77.3	0.8078	1.2019	0.1291
77.2	.8081	1.2021	.1292
74.1	.8220	1.2053	.1311
72.4	.8296	1.2074	.1324
69.3	.8431	1.2104	.1342
68.2	.8478	1.2121	.1352
66.3	.8563	1.2140	.1364
65.5	.8592	1.2150	.1370
63.5	.8677	1.2171	.1383
$\lambda = 5461$ Å			
77.3	0.8078	1.1990	0.1273
77.2	.8081	1.1993	.1275
74.1	.8220	1.2026	.1295
72.4	.8296	1.2042	.1305
69.2	.8435	1.2080	.1327
$\lambda = 5461$ Å—*Continued*			
68.3	0.8473	1.2092	0.1335
66.3	.8563	1.2111	.1347
65.5	.8592	1.2121	.1352
63.5	.8677	1.2144	.1367
$\lambda = 6939$ Å			
77.2	0.8081	1.1980	0.1267
75.1	.8176	1.1999	.1279
73.8	.8238	1.2015	.1288
70.9	.8361	1.2045	.1307
68.4	.8469	1.2068	.1321
65.5	.8592	1.2101	.1340
63.5	.8677	1.2121	.1353

The refractive indices for nitrogen at the normal boiling point, 77.38° K. (see graph), are: $\lambda = 4358$ Å, 1.2019; $\lambda = 5461$ Å, 1.1990; $\lambda = 6939$ Å, 1.1977.

As in the case of oxygen the results are not in error more than ± 0.0005. It can be seen from the graph that none of the points deviate by more than

this amount from the lines. Dewar and Liveing (4) obtained the value 1.2053 for the sodium D line with nitrogen at a temperature of −190° C. The value that is given in the International Critical Tables for nitrogen at the normal boiling point is 1.1975 for 5790 Å, which is in fairly good agreement with that obtained by the authors.

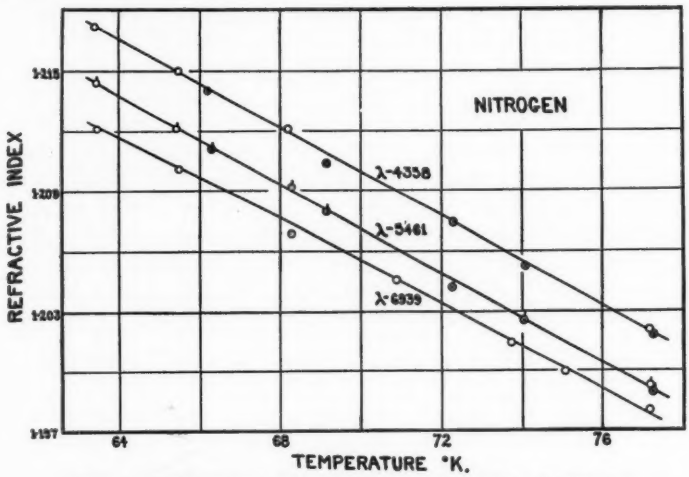


FIG. 4. *The temperature-refractive index diagram for liquid nitrogen.*

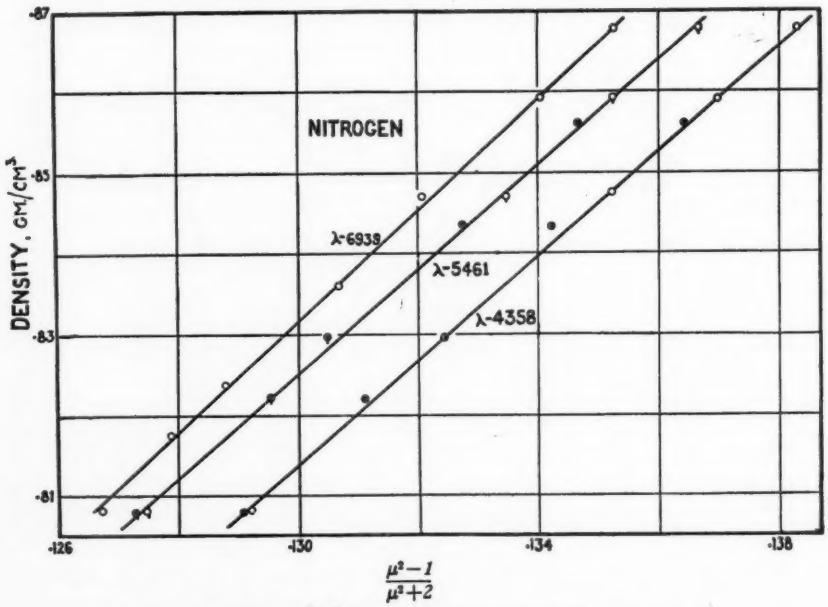


FIG. 5. *The function* $\frac{\mu^2-1}{\mu^2+2}$ *plotted against the density for liquid nitrogen.*

Hydrogen

The results for hydrogen are given in Table III and are represented graphically in Figs. 6 and 7. Owing to the fact that the hydrogen became slightly cloudy at the lower temperatures a complete set of measurements could not be made for 6939 Å.

TABLE III

THE REFRACTIVE INDICES OF LIQUID HYDROGEN BOILING AT DIFFERENT TEMPERATURES

Temp., ° K.	Density (9), gm. per cc.	Refractive index	$\frac{\mu^2-1}{\mu^2+2}$
λ=4358 Å			
20.39	0.07085	1.1142	0.07447
19.56	.07175	1.1156	.07538
18.96	.07239	1.1170	.07627
17.97	.07341	1.1184	.07715
17.22	.07415	1.1199	.07811
16.01	.07529	1.1215	.07912
15.58	.07568	1.1226	.07982
14.01	.07709	1.1244	.08096
λ=5461 Å			
20.39	0.07085	1.1121	0.07315
19.56	.07175	1.1134	.07398
18.96	.07239	1.1148	.07487
λ=5461 Å—*Continued*			
18.00	0.07338	1.1166	0.07601
17.45	.07392	1.1169	.07620
17.13	.07424	1.1184	.07716
16.50	.07484	1.1187	.07735
16.02	.07528	1.1199	.07811
14.01	.07709	1.1221	.07950
λ=6939 Å			
20.39	0.07085	1.1108	0.07232
19.56	.07175	1.1121	.07315

The best values for the refractive indices of hydrogen at the normal boiling point, 20.41° K., are: λ=4358 Å, 1.1141; λ=5461 Å, 1.1120; λ=6939 Å, 1.1107.

An error of two minutes in the critical angle would introduce an error of ±0.0003 in the value of the refractive index for hydrogen. As can be seen

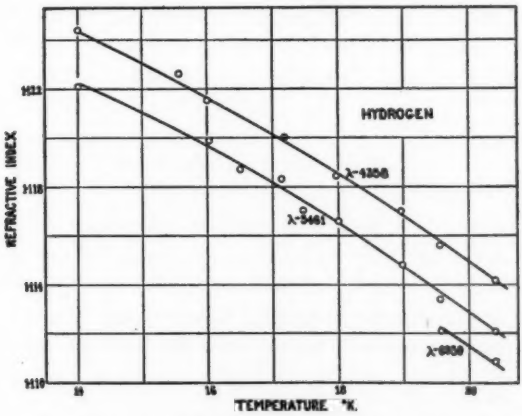


FIG. 6. *The temperature-refractive index diagram for liquid hydrogen.*

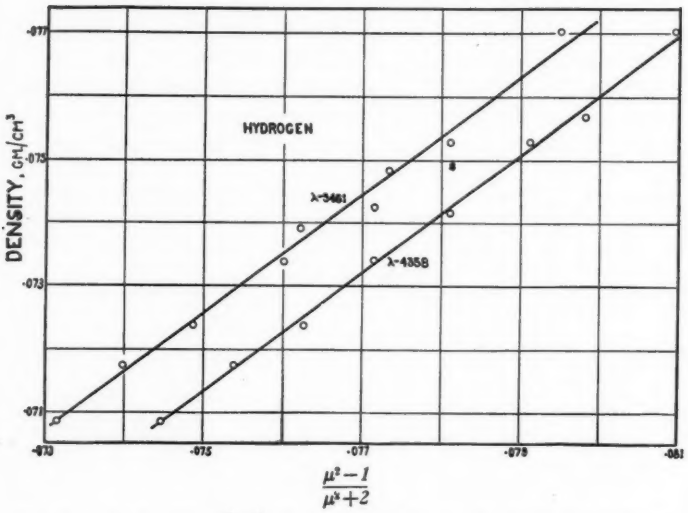


FIG. 7. *The function* $\frac{\mu^2-1}{\mu^2+2}$ *plotted against the density for liquid hydrogen.*

from the graph few of the points deviate by more than this from the line. It is therefore likely that the errors in these determinations are less than ± 0.0003. These values are low as compared with the value 1.12 obtained by Dewar (2), and high as compared with 1.097 as given in the International Critical Tables for 5790 Å.

Acknowledgments

The authors wish to take this opportunity to thank Prof. E. F. Burton, Director of the McLennan Laboratory, and Prof. H. Grayson Smith for the interest they have shown throughout the research. Acknowledgments are also due to Mr. A. I. Cove for the preliminary work which he did in 1935–1936, and Mr. R. H. Chappell for his splendid glass blowing.

References

1. BALY, E. C. C. and DONNAN, F. G. J. Chem. Soc. 81 : 907-923. 1902.
2. DEWAR, SIR JAMES. Collected papers. Vol. 2. Cambridge University Press. 1927.
3. DEWAR, J. and LIVEING, G. D. Phil. Mag. 34 : 205-209. 1892.
4. DEWAR, J. and LIVEING, G. D. Phil. Mag. 36 : 328-331. 1893.
5. DEWAR, J. and LIVEING, G. D. Phil. Mag. 40 : 268-272. 1895.
6. MATHIAS, E. and ONNES, H. K. Leiden Communications, 117. 1911.
7. MATHIAS, E., ONNES, H. K. and CROMMELIN, C. A. Leiden Communications, 145c. 1915.
8. OLSZEWSKI, K. and WITKOWSKI, A. W. Bull. l'acad. Cracovie, 246, July, 1894.
9 ONNES, H. K. and CROMMELIN, C. A. Leiden Communications, 137a. 1913.

THE COEFFICIENT OF HEAT TRANSFER FOR VERTICAL SURFACES IN STILL AIR[1]

By R. Ruedy[2]

Abstract

For a vertical plane surface in still air the coefficient of heat transfer, valid within the range of temperatures occurring in buildings, depends on the temperature and the height of the surface. If black body conditions are assumed for the heat lost by radiation, the coefficient is equal to 1.39, 1.50, 1.62, and 1.73 B.t.u. per sq. ft. per ° F. at 32°, 50°, 68°, and 86° F. respectively, the height of the heated surfaces being 100 cm. Convection is responsible for about one-third, and radiation, mainly in the region of 10 microns, for about two-thirds of the heat loss. Convection currents depend on the temperature difference, while radiation depends on the average temperature. When attempts are made to stop convection currents by placing obstacles across the surface, the loss of heat due to natural convection varies inversely as the fourth root of the height, providing that the nature of the flow of air remains unchanged.

Introduction

Little attention is paid to the various factors contributing to the flow of heat when the heat lost through windows is measured. The form of the flow of heat becomes too complicated to be established by measurements alone, so that it is useful to study a relatively large vertical surface as a standard with which surfaces having cross bars and other obstacles may be compared.

The single window behaves like any other partition that is in contact with warm air of temperature t_i on the inside and with cold air of temperature t_o on the outside. In order that a steady transfer of heat may take place, appropriate temperature differences must establish themselves between (i) the mass of warm air and the inner surface of the window, (ii) the two glass surfaces, (iii) the outer surface of the pane and the atmosphere. Because the decrease in temperature across windowpanes is small, the transfer of heat between the air and the glass is most important, and is no longer a quantity for which an approximate value may be introduced, as in thick walls, without appreciably changing the results.

Natural Convection

The windowpane gains and loses heat by radiation and by natural convection. The cold air that is in contact with its outer surface is heated by the warmer glass surface, rises to the top of the window, and along the walls until it has lost the heat that it has gained. Near the bottom of the warm glass surface the difference in temperature between the glass and outside air is large and, hence, the air is heated rapidly.

[1] *Manuscript received March 23, 1937.*
Contribution from the Division of Research Information, National Research Laboratories, Ottawa, Canada.
[2] *Research Investigator, National Research Laboratories, Ottawa.*

When the windows and the walls are in practically the same vertical plane, and when the temperature differences are not too large, the flow of these convection currents obeys the equations for laminar conditions (6, 7):

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0$$

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_y}{\partial y} = \nu \frac{\partial^2 v_y}{\partial x^2} + g\left(\frac{T}{T_e} - 1\right) = \nu \frac{\partial^2 v_y}{\partial x^2} + g \frac{T_w - T_e}{T_e} \theta$$

$$v_y \frac{\partial \theta}{\partial y} + v_x \frac{\partial \theta}{\partial x} = a \frac{\partial^2 \theta}{\partial x^2}$$

in which,

v is the velocity of the air at any point x, y,
T is the temperature (° K.) at any point x, y,
T_w is the temperature (° K.) of the wall,
T_e is the temperature (° K.) of the mass of outside air,
$\theta = \dfrac{T - T_e}{T_w - T_e}$,
g is the constant of gravity,
a is the diffusivity of the air,
ν is the coefficient of kinematic viscosity.

After the introduction of the independent variable

$$\eta = \sqrt[4]{\frac{g}{4\nu^2}\left(\frac{T_w}{T_e} - 1\right)} \frac{x}{\sqrt[4]{y}},$$

the solution of the system of equations may be expressed by two functions of η and their derivatives,

$$\theta = X(\eta),$$

$$v_y = 4\nu \sqrt{\frac{g}{4\nu^2}\left(\frac{T_w}{T_e} - 1\right)}\, \Gamma(\eta).$$

The functions X and Γ are given by infinite series that satisfy the differential equations for the convection currents set up in the vertical direction y. The temperatures and the velocities, v_y, in a vertical direction, near a vertical surface kept at the temperature t_w, are plotted in Figs. 1 to 4, for three cases that often occur in practice.

The corresponding equations are,

$$v_y = 17\sqrt{y}\,\Gamma\left(5.5 \frac{x}{\sqrt[4]{y}}\right) \quad t = 20\, X\left(5.5 \frac{x}{\sqrt[4]{y}}\right) \text{ for } \begin{matrix} t_w = 20° \text{ C.} \\ t_e = 0° \text{ C.} \end{matrix}$$

$$v_y = 12.2\sqrt{y}\,\Gamma\left(4.87 \frac{x}{\sqrt[4]{y}}\right) \quad t = 10\, X\left(4.87 \frac{x}{\sqrt[4]{y}}\right) \text{ for } \begin{matrix} t_w = 0° \text{ C.} \\ t_e = -10° \text{ C.} \end{matrix}$$

$$v_y = 22\sqrt{y}\,\Gamma\left(6.77 \frac{x}{\sqrt[4]{y}}\right) \quad t = 30\, X\left(6.77 \frac{x}{\sqrt[4]{y}}\right) \text{ for } \begin{matrix} t_w = 0° \text{ C.} \\ t_e = -30° \text{ C.} \end{matrix}$$

The curves obtained show that at any height, y, the vertical velocity, v_y, of the natural convection currents, increases rapidly with the distance in the first few millimetres from the wall. Near the bottom of the vertical surface the maximum velocity is reached within less than 3 mm. from the wall, and near the top, within less than 6 mm. Beyond these points the velocity of the natural convection currents decreases nearly as rapidly as it increased. When, therefore, two surfaces are placed face to face so as to leave an air gap between them, the convection currents will be disturbed more near the top of the gap than near the bottom. A large reduction of the velocity of the air currents in a gap takes place only when the two solid surfaces are set closer than about 1.25 cm. or as close as 0.5 cm., depending upon the height.

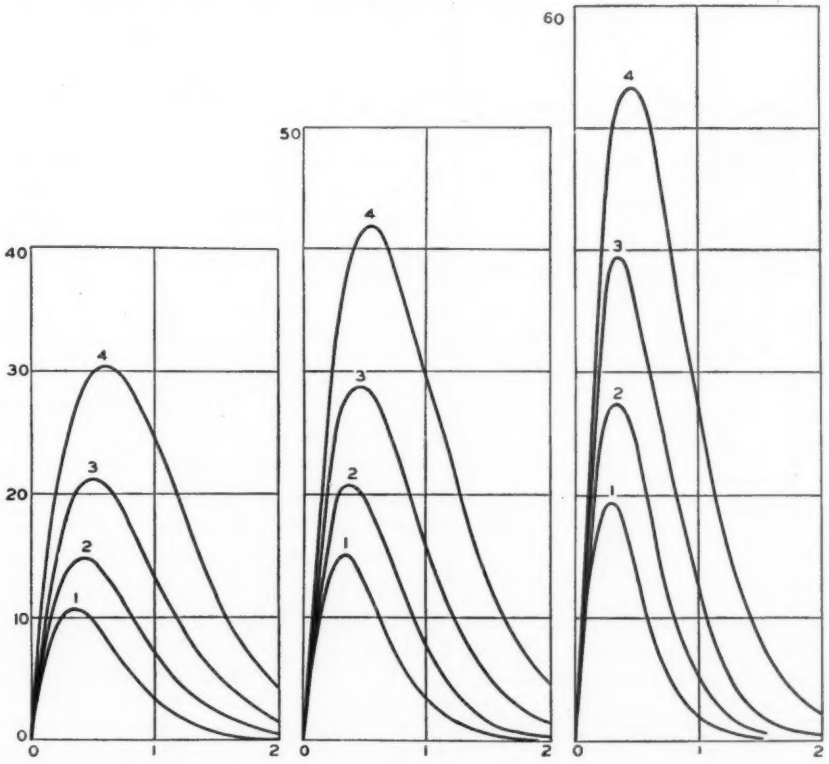


FIG. 1. FIG. 2. FIG. 3.

Vertical velocity (ordinates), in cm. per sec., of the convection currents at the distance x (abscissas), in cm., from a vertical wall heated in still air, and at four different heights y (10, 20, 40, and 80 cm., Curves 1, 2, 3, and 4). The temperature of the heated portion of the wall is t_w, that of the outside air, t_a.

FIG 1. $t_w = 0°$ C. $t_a = -10°$ C. FIG. 2. $t_w = 20°$ C. $t_a = 0°$ C. FIG. 3. $t_w = 0°$ C. $t_a = -30°$ C.

With increasing distance, x, from the surface, the temperature decreases quite rapidly at the bottom of the surface, and more slowly near the top; and, to within a few degrees, the outside temperature is reached at 1 cm. from the vertical surface. The increased loss of heat that natural convection produces may, therefore, be illustrated by comparing the loss due to convection with the heat conductivity of air, since this figure refers to a drop of one degree per unit length.

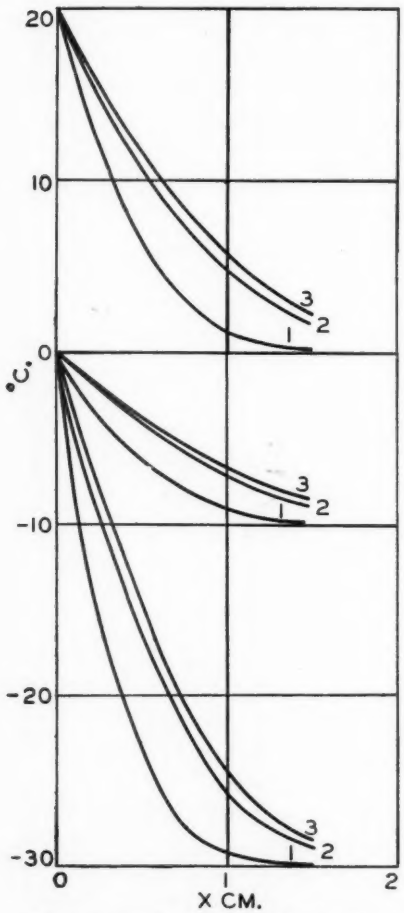


FIG. 4. *Temperature at heights 10, 80, and 120 cm. above the bottom edge (Curves 1, 2, and 3 respectively) at the distance x from a vertical wall heated in still air.*

The transfer of heat per unit surface per unit degree difference in temperature ($t_w - t_e = 1$) is equal to

$$k = -\lambda \frac{\partial \theta}{\partial x} \quad \text{at } x = 0 \text{ (wall)}$$

$$\text{or } k = -\lambda X'_w \cdot \sqrt[4]{\frac{g}{4\nu^2}\left(\frac{T_w}{T_e} - 1\right)\frac{1}{y}}$$

at any point of the boundary. Integrating between $y=0$ and $y=h$ and taking the average gives the value in Calories per square metre per hour per degree Centigrade,

$$k_m = -\frac{4}{3}\lambda X'_w \cdot \sqrt[4]{\frac{g}{4\nu^2 h}\left(\frac{T_w}{T_e} - 1\right)}$$

$$= 4.8 \sqrt{\frac{b}{760}} \sqrt[4]{\frac{T_w - T_e}{h\, T_e}}, \quad (1)$$

where b is the barometric pressure in millimetres of mercury, λ is the coefficient of heat conductivity of the air, and $X'_w = 0.021$.

The average surface coefficient is large when T_w/T_e is large and when the height of the warm surface is small. It is proportional to the fourth root of $(T_w - T_e)/T_e$ and inversely proportional to the fourth root of the height, h. The height, therefore, exerts a relatively small influence. The temperature enters into the formula for k not only as a function of the temperature difference between the walls and the outside air, but also as a function of the temperature of the outside air. For the temperatures likely to obtain near windows, $-50°$ to $+50°$ C., the temperature difference exerts the greatest influence as may be seen from Table I.

TABLE I

VALUES OF $\sqrt[4]{\frac{T_w - T_e}{T_e}}$ FOR VARIOUS VALUES OF t_w AND t_e (° C.)

t_e, ° C.	t_w, ° C.					
	0	10	20	30	40	60
−20	0.530	0.586	0.636			
−10	0.442	0.525	0.581	0.625	0.660	
0		0.437	0.520	0.576	0.618	
10			0.433	0.516	0.571	0.648
20				0.430	0.511	0.615
30					0.426	0.561
40						0.503
						0.421

For the normal range within which Formula (1) is employed in practice the various other variables are given in Table II.

TABLE II

AUXILIARY VALUES

T_e, ° K.	$T_e^{-\frac{1}{4}}$	h, m.	$h^{\frac{1}{4}}$, m.	$t_w - t_e$, ° C	$\left(\frac{T_w - T_e}{T_e}\right)^{\frac{1}{4}}$
263	0.248	0.25	0.707	5	0.37
273	0.246	0.5	0.841	10	0.44
283	0.244	1	1	15	0.49
293	0.242	2	1.19	20	0.53
303	0.240	3	1.32	30	0.59
		4	1.414	40	0.63

The transfer of heat, H, in Calories per square metre per hour caused by natural convection is

$$H = \frac{4.8}{\sqrt[4]{h}} \sqrt[4]{\frac{T_w}{T_e} - 1} \ (t_w - t_e).$$

The tables show that as far as natural convection is concerned, the surface coefficient used in formulas of the type

$$H = \frac{kc}{\sqrt[4]{h}} \ (t_w - t_e)$$

becomes actually a function of the temperature difference only. For heights of one metre and temperatures between −20° and +40° C. the coefficients are given in Table III.

TABLE III

SURFACE COEFFICIENTS, k, DETERMINED BY NATURAL CONVECTION

Units	Temp. difference			
	5°	10°	20°	30°
Cal. per sq. m. per hr. per ° C.	1.76	2.12	2.55	2.84
B.t.u. per sq. ft. per hr. per ° F.	0.36	0.43	0.52	0.58

These coefficients should be compared with the thermal conductivity of air, in the absence of convection, namely 0.144, 0.156, and 0.168 B.t.u. per sq. ft. per hr. per ° F. at the temperatures 0°, 32°, and 100° F., respectively.

The fact that the heat carried away from a warm surface by natural convection varies inversely as the fourth root of the height was pointed out more than 50 years ago (3), and has been rediscovered from time to time (4). In an air gap the result obtained depends, however, on the width of the gap.

For a temperature difference of 50° F. across gaps 1.5 in. wide and 9 in. and 35 in. in height, the coefficients for both surfaces combined are 0.44 and 0.309 respectively (4). The ratio of the coefficients is 1.42; the fourth root of the inverse ratio of the height is 1.48. When the width is reduced to 0.8 in. the ratio of the coefficients is 0.42 : 0.28, or 1.50. The agreement remains satisfactory until spaces less than 0.4 in. wide are considered; with narrower gaps the ratio begins to decrease from the value 1.42 (that is, 0.47/0.33) toward unity. For gaps less than 4 in. in height the conditions outside the gap become as important as the height.

The theory used assumes that the heated surface is set flush into a large wall at uniform temperature, so that the air taking part in the convection arrives and leaves in laminar flow at the bottom and top. When the warm surface is freely suspended in a room the transfer of heat is greater, the coefficient 6.12 replacing the value $0.848\ \lambda/\nu^{\frac{1}{4}}$, which is equal to 4.8 for all temperatures between −50° C. and +50° C. (8). A larger coefficient is probably also valid when the temperature differences increase and the flow becomes turbulent.

The resistance that the flowing air has to overcome in order to reach the surface accounts for the fact that the formulas do not apply accurately to horizontal surfaces, although in practice the difference is negligible.

Heat Loss by Radiation

The radiation from a window in the wall of a room depends on the temperature of the glass, the temperature of the surroundings, the ratio of the area of the window to the area of the surface towards which the window radiates, the nature of this surface, and upon the wave-length of the radiation. In a house that is nearly free on all sides, the window faces the atmosphere and the ground; if these surroundings act as a black body the loss of heat reaches its largest value, and is given, in calories per square centimetre per second by

$$H = 1.37 \times 10^{-12}\, e_1\, (T_w^4 - T_e^4)\ ,$$

where T_w and T_e are measured in ° K.; and in the English system of units by,

$$H = 0.172\, e_1 \left(\left(\frac{T_w}{100} \right)^4 - \left(\frac{T_e}{100} \right)^4 \right).$$

In these formulas, e_1 is the emissivity of the surface or the emission expressed as a fraction of the amount of energy that the black body would emit at the

same temperature. For the wave-lengths emitted by the warm glass, mainly about 10 microns, glass absorbs quite strongly (1); and its emissivity, e_1, at long wave-lengths is between 0.9 and 1.0.

It is convenient to express the heat that the glass loses from unit area in unit time by the formula

$$H = \frac{5.93}{10^8} \frac{T_w^4 - T_e^4}{T_w - T_e} (T_w - T_e)\, e_1 = 5.93 e_1\, a(t_w - t_e)$$

the units being Calories per square metre per hour.

If the temperatures remain much below 460° F. (273° C.), the fraction $(T_1^4 - T_2^4)/(T_1 - T_2)$ depends only on the average temperature $(T_1 + T_2)/2$, since,

$$10^8 a = \frac{T_1^4 - T_2^4}{T_1 - T_2} = (T_1 + T_2)^3 \left(1 - \frac{2T_1 T_2}{(T_1 + T_2)^2}\right) \doteq 4\left(\frac{T_1 + T_2}{2}\right)^3.$$

TABLE IV

SURFACE COEFFICIENTS DUE TO RADIATION AT THE AVERAGE TEMPERATURE $\frac{T_1+T_2}{2}$

°C.	−15	−10	−5	0	5	10	15	20
a	0.69	0.729	0.772	0.816	0.86	0.91	0.96	1.0
$5.93a$	4.09	4.32	4.58	4.84	5.09	5.40	5.69	5.93
°F.	5	14	23	32	41	50	59	68
$0.172a$	0.838	0.885	0.939	1.0	1.043	1.107	1.166	1.215

The coefficients thus calculated may be used to express the heat loss from the surface due to radiation as a function of the temperature difference in the form

$$H = e_1\, k_r\, (t_w - t_e).$$

The Surface Coefficient in Still Air

The contributions that natural convection and radiation make to the surface coefficient at various temperatures are shown in Table V.

Radiation is responsible for about two-thirds and convection for about one-third of the heat loss. Moreover, since for a given temperature of the warm surface, the average temperature and the radiation increase with increasing outside temperature, while the temperature difference and the amount of convection decrease with increasing outside temperature, the two influences are in opposite direc-

TABLE V

SURFACE COEFFICIENTS AS DETERMINED BY RADIATION (UPPER FIGURE) AND CONVECTION (LOWER FIGURE)

t_e, °C.	t_w, °C.			
	0	10	20	30
−20	4.32 2.55	4.58 2.84		
−10	4.58 2.12	4.84 2.55	5.09 2.84	
0		5.09 2.12	5.40 2.55	5.69 2.84
10			5.69 2.12	5.93 2.55
20				6.13 2.12

tions and in fact practically cancel each other (Table V). The surface coefficient of a vertical surface becomes a function of the temperature of the warm surface throughout the range of temperatures encountered in the course of the year.

If the coefficients are divided by 4.88, the values to be used with the units B.t.u., ft., ° F. are obtained. For black surfaces ($e_1 = 1$) 100 cm. high, the surface conductances are 1.39, 1.50, and 1.62 B.t.u. per sq. ft. per hr. per ° F. at a wall temperature of 32°, 50°, and 68° F., respectively.

TABLE VI

SURFACE COEFFICIENTS (CALORIES PER SQUARE METRE PER HOUR PER DEGREE DIFFERENCE) AS A FUNCTION OF THE EMISSIVITY e_1

e_1	t_w, ° C.			
	0	10	20	30
1.0	6.79	7.34	7.90	8.42
0.8	5.89	6.37	6.82	7.23
0.6	5.00	5.40	5.74	6.05
0.4	4.10	4.43	4.66	4.87
0	2.84 to 2.12			

The value used in practice has been increased from 1.50 to 1.65 in articles and books dealing with heating and ventilating published in the last few years. It would have been more correct to adopt a coefficient that depends upon the temperature of the surface. However, since still air conditions usually obtain inside the house, the value of 1.65 is valid where it may be assumed that the surface behaves as a black body in surroundings that may be considered also as black bodies. Walls are not black bodies, and a certain fraction, f, of the radiation is returned, and absorbed by the surface. In the laboratory, windows are tested while forming a cover to a box that is of the same size as the window, cover and bottom being separated by a distance that is smaller than the dimension of the window surface. In this case the heat loss, H, is only the fraccion $e_1 e_2/(e_1 + e_2 - e_1 e_2)$ of what it would be with black bodies.

The theory also indicates that the surface coefficient to be used for entire walls is appreciably smaller than the coefficient applying to surfaces not larger than ordinary windowpanes. Under these conditions measurements on an arbitrary vertical surface or window are unlikely to furnish a coefficient valid in the general case.

Heat Transfer by Forced Convection between a Plane Surface and a Stream of Air

A much larger amount of heat is lost when the wind blows in a direction parallel to the surface of the window. Theory and experiment lead to the formula

$$Q = 0.0356\, c\, V\, (Re)^{-\frac{1}{4}}\, (t_w - t_a)$$

where Q is the heat lost in Calories per second per metre width,

c is the specific heat per unit volume at constant pressure,

V is the velocity of the wind in metres per second,

Re is Reynolds' number; $\dfrac{\text{velocity} \times \text{length of the plate}}{\text{kinematic viscosity}}$.

When the hour is taken as the unit of time, the formula may be written

$$Q = 5\ V^{\frac{1}{2}}\ l^{-\frac{1}{4}}\ (t_w - t_a)\ .$$

The length, l, exerts only a slight influence, and in the neighborhood of 1 m. the surface coefficient may be considered as constant. Its value for $l=1$ is given in Table VII.

TABLE VII

SURFACE COEFFICIENT, k_v, OF FORCED CONVECTION
(neglecting the factor $l^{-\frac{1}{4}}$)

Wind velocity, m. per sec.	2	3	4	5	6	7	8	9	10
Q, Cal. per sq. m. per ° C.	8.71	12.4	15.2	18.1	21.0	23.7	26.4	29.0	31.6
Q, B.t.u. per sq. ft. per ° F.	1.78	2.55	3.18	3.72	4.3	4.9	5.4	5.9	6.5
Wind velocity, miles per hr.	4.47	6.71	8.94	11.19	13.42	15.69	17.9	20.1	22.4

The heat loss from the surface is equal to the amount of heat carried away by (i) forced convection as determined by the coefficient k_v, and (ii) the heat given off by radiation and determined by the coefficient k_r at various average temperatures. The old value for the surface coefficient recommended for a wind of 15 miles per hr. is decidedly too low according to the theoretical and laboratory results, since k_v alone is equal to 4.7 B.t.u. per sq. ft. per ° F., and k_r may increase this value to nearly 6 units. This is the value now used in practice and is probably correct for windows, but certainly too large when applied to entire outside walls. Experience also shows that in winds with a speed of 5 m. per sec. or more the flow of the air is no longer steady.

References

1. BLACKSHAW, J. L. and HOUGHTON, F. C. Heating-Piping, 5 : 523-525. 1933.
2. ELIAS, F. Abh. Aerod. Inst. Aachen, 9 : 10-39. 1930.
3. FISHENDEN, M. and SAUNDERS, O. A. Calculation of heat transmission. H. M. Stationery Office, London. 1932.
4. QUEER, E. R. Heating-Piping, 3 : 960-965. 1931.
5. ROWLEY, F. B. and ALGREN, A. B. Heat transmission through building materials. Bull. No. 8, University of Minnesota, Eng. Exp. Sta. 1932.
6. SCHMIDT, E. and BECKMANN, W. Tech. Mech. Thermodynam., 1 : 341-349. 1930.
7. SCHMIDT, E. and BECKMANN, W. Tech. Mech. Thermodynam., 1 : 391-406. 1930.
8. WEISE, R. Forsch. Gebiete Ingenieurw. 6 : 281-292. 1935.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 15, SEC. B. JULY, 1937 NUMBER 7

AN INVESTIGATION OF THE CHLORINATION OF SPRUCE WOOD AND OF THE RESULTING CHLOROLIGNIN[1]

BY G. V. JANSEN[2] AND J. W. BAIN[3]

Abstract

Spruce sawdust was chlorinated under various conditions in an attempt to procure a homogeneous lignin chloride. Success finally attended the use of methyl alcohol as a medium for chlorination. The lignin chloride, which was dissolved by the alcohol during the chlorination and subsequently precipitated by the addition of water, was cream white in color, and analysis showed it to be an alcohol lignin.

A homogeneous fraction (No. 2) was obtained from the re-chlorinated product, and it proved to be a chlorinated analogue of Hibbert's monomethylated methyl alcohol lignin, the formulas of the two products being $C_{42}H_{22}O_6Cl_{13}(OH)_3(OCH_3)_7$, and $C_{42}H_{32}O_6(OH)_3(OCH_3)_7$. The molecular weight and the presence of the two hydroxyl groups were confirmed by acetylation, when 2.0 acetyl groups entered the molecule. Eleven of the chlorine atoms in Fraction 2 have evidently replaced ten hydrogen atoms and one hydroxyl group by simple substitution in methyl alcohol lignin, leaving two chlorine atoms which have apparently entered to saturate a double bond. Seven of these chlorine atoms have been shown to be readily removable either by an alkali or by acid reduction. The other six, because of their stable union with the molecule, are surmised to be joined to an aromatic nucleus or at least to some type of ring structure. The product has been shown to react stoichiometrically within limits as narrow as could be expected for such a large molecule.

Introduction

One of the less severe methods by which lignin can be isolated from wood was discovered by Cross and Bevan in 1880 (3). They chlorinated moist jute fibre and extracted the chlorinated lignin with hot alcohol, from which solution it was precipitated by dilution with water as a yellow amorphous powder. This paper deals with an investigation of this method of isolating lignin and of the chlorolignin so obtained. The results of other investigators who have studied the halogenation of wood or lignin are briefly summarized in the following section.

Cross and Bevan (3) invariably obtained, from the chlorination of moist jute, a lignin chloride of the composition represented by $C_{19}H_{18}Cl_4O_9$ (Cl, 26.8%). The amount of hydrochloric acid formed was equivalent to the chlorine absorbed. This denoted simple substitution of hydrogen by chlorine. However, for fibres other than jute, hydrochloric acid was formed in excess; this showed that oxidation had taken place (5, p. 105). On further chlorination in acetic acid solution (4), the substance $C_{38}H_{44}Cl_{11}O_{16}$ was obtained (Cl, 34%).

[1] *Manuscript received December 29, 1936.*
Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Canada.

[2] *Research Assistant, School of Engineering Research, University of Toronto.*
[3] *Professor of Chemical Engineering, University of Toronto.*

Heuser and Sieber (15) chlorinated moist pine sawdust and found that 32% of hydrochloric acid was formed, whereas only 9.47% of chlorine combined with the wood. (These percentages refer to the weight of dry wood used, as will all succeeding percentage figures unless otherwise specified.) By means of alcoholic extraction they obtained a substance that gave the following analysis: Cl, 22.68%; C, 47.03%; H, 4.59%. The yield was only 7.1%. (Pine and spruce contain about 30% lignin.)

Heuser and Casseus (14) found that dry spruce wood flour suspended in carbon tetrachloride was acted upon by chlorine; with moist wood the reaction was more rapid. They could extract all the lignin in either case by successive treatments with sodium sulphite solution. The chlorine absorbed amounted to 41% of the weight of the wood, as was found by Heuser and Sieber.

Waentig (26) chlorinated wood-meal suspended in water; he stated that no chlorination took place in the absence of moisture. By alcoholic extraction he obtained lignin chlorides in which the chlorine content varied from 25.5 to 38.9%, depending directly upon the duration and temperature of chlorination and the acidity (hydrochloric acid) of the chlorination medium.

Moreover, the chlorine content of the alcoholic extract from any one experiment was not uniform. A water soluble lignin chloride was also produced in which the chlorine content varied from 18.6 to 19.1%.

Recently Müller (19) extensively investigated chlorolignin. He chlorinated moist pine sawdust and extracted the still moist wood, which then contained hydrochloric acid, with boiling 90% alcohol. If the wood were washed free of acid before extraction, only a small yield of lignin was obtained. This showed that a hydrolytic cleavage of the ligno-cellulose bond was necessary. The chlorinated lignin was precipitated as a golden brown colloid when the alcoholic solution was diluted with water. Müller separated the lignin chloride into two fractions by ether extraction:

(1) Ether insoluble lignin chloride, Cl, 23.1; OCH_3, 4.5%.
(2) Ether soluble chlororesin, so called because it resembled resin in appearance; Cl, 28.6; OCH_3, 4.8%.

Extraction of the lignin chlorides with water, hydrolysis (acid or alkaline), oxidation with potassium permanganate, or dry distillation, yielded no information as to their structure. However, alkali fusion yielded succinic acid and terephthalic acid as degradation products, and Müller considers that this indicates that in lignin there is a benzene ring containing two adjacent carboxyl groups. He also prepared a monoamide of chlororesin, and thus confirmed the presence of at least one carboxyl group in lignin.

Powell and Whittaker (22, 23) chlorinated alkali lignin obtained from various woods, and found that 12 chlorine atoms entered the lignin molecule. On solution in alkali and reprecipitation with acid, six chlorine atoms were split off. They give the following formulas for these bodies:

Dodecachlorolignin—$C_{40}H_{20}O_8Cl_{12}(OH)_6OCH_3CHO$; Cl, 35.1 to 35.5%.
Hexachlorolignin—$C_{43}H_{38}O_{16}Cl_6$; Cl, 20.4 to 20.8%.

Taylor, Maass and Hibbert (25) studied the mechanism of aqueous halogenation of several unsaturated compounds, using hypochlorous and hypobromous acids and various catalysts. They have shown that the addition of these acids to a double bond is in general catalyzed by undissociated hydrochloric and hydrobromic acids. They also studied the aqueous halogenation of phenols under the above conditions. Applying like methods to an investigation of the reaction of hypochlorous acid on glycol-lignin, Hibbert and Taylor (17) conclude that there is about 15% of a phenol nucleus in lignin, which accounts for about one-third of the rapid absorption of hypochlorous acid observed. The remainder they ascribe to the addition of hypochlorous acid to an ethylene linkage, chlorination of a phenol ether, or a combination of both reactions.

Some of the results of work done on the bromination of wood and lignin are of interest in connection with this paper and will be briefly outlined. Fuchs (9, 10, 11,) brominated spruce wood, Willstätter lignin, and acetylated spruce wood, and concluded that primary lignin contains a hydrogen atom that is replaceable by bromine and a double bond capable of addition of two bromine atoms, and that acetate lignin contains a tetrahydro benzene ring. Hibbert and Sankey (16) also found that lignin contained one or more double bonds per mole. Rassow and Zickman (24), on the other hand, conclude that there are no double bonds in Willstätter lignin. Friedrich and Pelikan (8) brominated lignin, extracted by acetic acid, in alcohol, acetic acid, and alkali solution. In alcohol solution, only an addition of bromine occurred and no methoxyl was split off. In alkali solution extensive oxidation took place, but in acetic acid a maximum bromine content of 38.7% was reached in 12 hr. Since the methoxyl content had dropped from 15.5 to 10.6% they concluded that the methoxyl groups in lignin are not all of the same type, and that the methoxyl groups split off during bromination remain as hydroxyl groups.

It can be seen that there is considerable disagreement in the results summarized above, and that no two of the various empirical formulas proposed for lignin agree. Nor does any one of these formulas for a lignin isolated by chlorination or bromination bear a close resemblance to those for lignin isolated by any of the other well known methods. However, by means of a suitable method of chlorination, the authors have succeeded in isolating a lignin fraction that appears to be a chlorinated derivative of Hibbert's monomethylated alcohol lignin.

General Procedure

Ontario white spruce only was used in the work described below. It was ground to pass a 100 mesh screen and extracted with a minimum boiling point mixture of benzene and ethyl alcohol for 20 hr. to free it from resins. After air-drying, its moisture content was determined and the dry weight calculated. It was then placed in the chlorinating apparatus, being either bone-dried or well moistened before chlorination.

Two types of chlorinating apparatus were used. The apparatus used first is shown in Fig. 1. Either pure chlorine gas or chlorine diluted with air, to keep the temperature low, could be drawn through the wood. Cooling to 0° C. could be achieved by the admission of ether or chloroform through the dropping funnel. (In these cases the wood was moistened with sodium nitrate solution to prevent its freezing.) The gas stream was led through the water in the bottom of the suction flask so that the hydrochloric acid that it carried from the wood might be absorbed. The wood was water washed after each chlorination till free from chlorides, and the hydrochloric acid was then determined by titration after removal of the chlorine in the wash water by the addition of sodium thiosulphate.

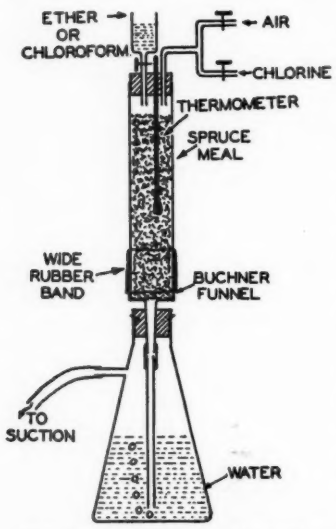


FIG. 1. *Apparatus for chlorination.*

The wood was then extracted with alcohol in a Soxhlet for several hours, and the alcoholic solution of lignin chloride was concentrated by distillation *in vacuo*. In the experiments in which the water-soluble lignin chloride was determined, the water extraction of the chlorinated wood was performed first, under reduced pressure, and the lignin chloride was recovered by distilling off the water *in vacuo*. This process was repeated several times, four chlorinations and extractions being usually found sufficient to exhaust the wood of all alcohol soluble lignin chloride. The lignin chloride was recovered from the concentrated alcoholic solution by precipitation with cold water. It was purified by redissolving and reprecipitating two or three times, the precipitate being washed free of chlorides each time.

After the lignin was freed from hydrochloric acid and adsorbed chlorine, it was frequently found necessary to employ a concentrated solution of an inorganic salt like sodium sulphate, to throw it out of colloidal suspension in the diluted alcoholic solution. After a final thorough washing with water, it was air dried and its moisture content determined.

The product so obtained was analyzed for chlorine by the explosion method in a Parr peroxide bomb. In this method approximately 0.2 gm. of sample is placed in a Parr bomb together with 0.5 gm. of pure maltose, to supply the water necessary to start the combustion, and 10 gm. of sodium peroxide. The bomb is then heated for 20 sec. with a full Bunsen flame, allowed to cool for a minute or so, plunged into cold water and the contents then rinsed out with distilled water. The resulting alkaline solution is acidified with nitric acid, filtered, and the sodium chloride is precipitated with silver nitrate and weighed as silver chloride. This method, which is quite rapid, has been

shown to be quite as accurate as the time-consuming Carius method even for high melting solids (1). Typical analyses were: Cl: 28.50, 28.60; 30.55, 30.60; 27.25, 27.25%.

The results of some of these experiments with the first apparatus are listed in Table I.

TABLE I

Experiment No.	Temp. of chlorination, °C.	Conditions	Hydrochloric acid formed, %	Loss in wt. of wood, %	Chlorine in residual wood, %	Yield of lignin chloride, %	Chlorine in lignin chloride, %
1	40	No cooling, only gaseous chlorine used.				7.0	22.50
2	40	No cooling, only gaseous chlorine used.				11.0	24.30
3	40	No cooling, only gaseous chlorine used. Wood was not washed with water prior to alcoholic extraction.		30.7	2.3	17.2	1st extr. — 20.55 2nd extr. — 21.75 3rd extr. — 23.05 4th extr. — 24.75
4	30	Chlorine mixed with air. Wood washed free of chlorides prior to alcoholic extraction.		16.0	3.0	4.9	14.6 to 18.6
5	0	Chlorine mixed with air. Wood washed free of chlorides prior to alcoholic extraction.	45.9	18.7	5.4	6.0	1st extr. — 21.25 2nd extr. — 23.45 3rd extr. — 23.10
7	0	Chlorine mixed with air. Wood washed free of chlorides prior to alcoholic extraction. Alcoholic extraction performed at reduced pressure.	33.0	17.4	6.6	6.4	1st extr. — 23.85 2nd extr. — 23.10 3rd extr. — 23.10 4th extr. — 23.40
8	30	Chlorine mixed with air. Wood washed free of chlorides prior to alcoholic extraction. Alcoholic extraction performed at reduced pressure.	34.1		4.0	6.4	1st extr. — 24.55 2nd extr.— 24.45 3rd extr.— 22.8 4th extr. — 23.5
9	50–60	Same as Experiment No. 3	96.5	20.9	4.4	13.4	1st extr. — 26.90 2nd extr.— 25.75
11	30	Same as Experiment No. 3		25.2	3.4	15.7	24.05

Discussion

The results in Table I are very similar to those obtained by Waentig (26) for his six hour chlorinations in a water medium, in which he obtained in 9% yield a lignin chloride with a chlorine content varying between 25.5 and 27.2%. As he concludes, the chlorine content of the lignin chloride varies with the chlorination temperature, the acidity, the duration of chlorination, and, to a certain extent, with the method of handling.

The amount of hydrochloric acid formed is high when no cooling is attempted, as would be expected. The greatest yields of lignin chloride were obtained in those experiments in which the wood was not water washed prior to alcoholic extraction. This showed that there is a considerable quantity of water soluble lignin chloride which is extracted during this process. That the chlorinated lignin cannot be completely extracted from wood by alcoholic extraction is shown by the fact that the residual wood invariably retains from 3 to 6% chlorine, which must be due to the lignin chloride it still contains.

The chlorine content of the water soluble lignin chloride obtained in Experiment 10 was 20.10%—lower than that of the alcoholic extract which was generally in the neighborhood of 24%.

The color of the lignin chloride seemed to vary also with the temperature of chlorination; that obtained from the chlorinations at 0° C. was bright yellow, whereas that obtained at higher temperatures was brown or gray. They all tended to darken on dry heating.

The product was soluble in alkali, ammonium hydroxide (dilute and concentrated), sodium carbonate solution (dilute and concentrated) and acetone (75% to absolute). It was partially soluble in glacial acetic acid, but on standing for some time it became insoluble in this reagent.

It was realized that conditions could not be controlled well enough to produce the same homogeneous product at will, so the apparatus shown in Fig. 2 was designed for chlorinating the wood in a liquid medium where the temperature could be better controlled, and local heating and attendant high oxidation eliminated.

Experiments with Apparatus No. 2

A chlorination was first attempted with dry wood flour (325 mesh) suspended in carbon tetrachloride. The wood absorbed 10.7% chlorine, but 26.7% of hydrochloric acid was formed. Considerable oxidation had therefore occurred. Less than 1% of the lignin chloride could be extracted by hot alcohol or acetone, and its chlorine content was not uniform, ranging from 13.5 to 32.5%. An experiment in which water soaked wood was used yielded more encouraging results; 20.6% of chlorine was absorbed and only 28% of hydrochloric acid was formed. This showed that little oxidation had taken place. The percentage of alcohol soluble lignin chloride recovered was 18, but this had a non-uniform chlorine content (28 to 32%). The methoxyl content of the

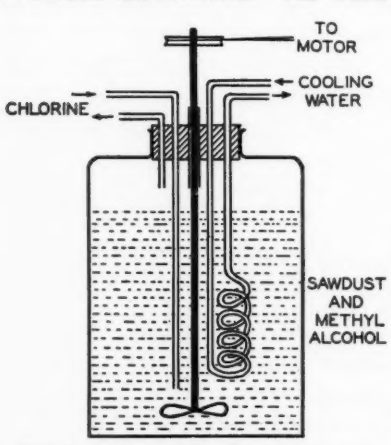


FIG. 2. *Apparatus for chlorination on a large scale.*

product was approximately 8.5% on a chlorine-free basis. Therefore, about one-half of the methoxyl content had been lost during chlorination (17% OCH_3 is the value assigned to spruce lignin by Brauns and Hibbert (2)).

Experiments on Chlorination in Methyl Alcohol

Since Friedrich and Pelikan (8) stated that they had obtained only an addition of bromine with no loss of methoxyl on brominating their lignin in alcohol, it was decided to try methyl alcohol as a medium for the chlorination of wood. The result was quite remarkable.

Air-dry wood (100 gm., 5% moisture content) was placed in 800 cc. of methyl alcohol and chlorinated for 48 hr. Neither the wood nor the alcohol was thoroughly dried, because it was desired to have a small amount of water present to facilitate the chlorination and increase the yield of lignin chloride, and it was felt that by using just this minimum amount, dissolved as it would be in the methyl alcohol, oxidation would be virtually eliminated.

After chlorination, the wood, which was still light yellow in color rather than orange (as in all previous experiments with moist wood), was filtered from the alcohol, washed free of chlorides, dried, and extracted with acetone *in vacuo*. This extraction yielded a cream yellow colored product (Cl, 29.6%) on precipitation with water. It was not possible to determine the amount of hydrochloric acid formed in this experiment, since the methyl alcohol was attacked by the chlorine.

The alcohol, which had been used for a chlorination medium, yielded an even lighter colored precipitate on addition of water, its color being virtually pure white and its chlorine content 28.8%. No other investigator has ever reported, to the authors' knowledge, a white colored lignin product. Alkali lignin perhaps comes the closest to this, being very light yellow. Grüss claims to have prepared a white crystalline lignin of formula $C_{26}H_{46}O_{10}$ (C, 60.2; H, 8.9%), by refluxing wood wet with hydrochloric acid solution with ethyl alcohol. However, Friedrich and Brüda (6) (see also (7)), though using this method to prepare their primary lignin, obtained a cocoa-brown colored product of empirical formula $C_{39}H_{48}O_{14}$ (C, 63.3; H, 6.5%). This analysis falls within the range generally given for lignin, whereas Grüss' compound is rather low in carbon and much too high in hydrogen. Grüss' "crystalline lignin" has hence never been reproduced. He did not give its methoxyl content. Friedrich and Diwald (7) gave 20.9% as the methoxyl content of their primary lignin, but Hägglund and Rosenquist (12) showed that part of this was due to ethoxyl, their product being a compound of ethyl alcohol and lignin or an "alcohol lignin" similar to the glycol lignins Hibbert and co-workers have recently been investigating (25). Calculated on the true weight of the lignin (less the ethoxyl part), the methoxyl content of primary lignin then becomes 14.0%, which is similar to the methoxyl content of Willstätter lignin. If the ethoxyl be replaced by methoxyl and the total methoxyl content be then considered, the methoxyl content would be 22.6%–

Brauns and Hibbert give as the methoxyl content of their methyl alcohol lignin 21.45%.

A further 12 hr. chlorination of the extracted wood in methyl alcohol yielded a white lignin chloride (Cl, 35.6%). The methoxyl content of the first extract of this white lignin chloride was 15.9%. Calculated on a chlorine-free basis (on the assumption that the chlorine atoms have replaced hydrogen atoms), this would be 22.1%, which indicated that this product was also an "alcohol lignin". However, the temperature required for its isolation is certainly much lower than that used in other methods for preparing such products, all those so far published depending on treatment of the wood with hot or boiling solvent plus hydrochloric acid for several hours, the resulting compound of lignin plus solvent being darker in color than that of the authors' (yellow, brown or gray).

The methoxyl content of the acetone extract was also high, *viz.*, 15.5, or 21.8% on a chlorine-free basis, so that evidently the alcohol combined with the lignin before it had been extracted from the wood.

Experiment on Alcohol Lignin Chloride

Air-dry wood (700 gm.) was chlorinated in methyl alcohol for a total period of three weeks. During this time the wood was allowed to settle about every four days and the supernatant layer of alcohol was siphoned off, the lignin that it contained being precipitated with cold water. The fifth extract yielded virtually no lignin, so the chlorination was assumed to be completed.

These extracts were united and washed with distilled water on a Büchner funnel till free of chlorides. The yield of crude, air-dry product was 122 gm., or 16.5% on a dry basis. The product was then redissolved in acetone and reprecipitated to further purify it. The only successful way of precipitating the lignin from this concentrated acetone solution was to dilute it with alcohol and then quickly add cold tap water, small portions being treated successively in this manner. If water was added directly to the acetone solution a brown, resinous mass came down, which, however, could be again obtained as the white product by the above technique of precipitation.

The product was then dried *in vacuo* over phosphorus pentoxide, and was further purified by redissolving it in acetone and precipitating it by the addition of carbon tetrachloride and then petroleum ether. The addition of petroleum ether alone again yielded a brown, gummy precipitate. A cream-white colored product (Cl, 29.8%) was thus obtained, the final yield being 55 gm. or about 8%.

The material was not homogeneous, as was shown by the analysis of two fractions obtained by adding carbon tetrachloride to an acetone solution, filtering and obtaining a second precipitate by the addition of petroleum ether. The chlorine contents of the two fractions were 27.4 and 30.0% respectively. Alcohol lignin chloride (20 gm.) was then rechlorinated in methyl alcohol for seven days. Most of the material, which had largely lost its solubility in this reagent during purification and drying, redissolved. The insoluble portion

was filtered off and the dissolved fraction recovered as before by precipitation with ice water. The chlorine content was now greater and much more uniform, as was shown by a test similar to that mentioned above, *viz.*: chlorine content of fraction precipitated by carbon tetrachloride, 31.5; chlorine content of fraction precipitated by petroleum ether, 31.9%. A second fractionation of the portion precipitated by petroleum ether yielded two fractions of almost identical chlorine content, namely 30.8 and 31.0%. Hence, it appeared that a homogeneous material could be obtained by fractional precipitation of the re-chlorinated alcohol lignin chloride, and to this end it was decided to prepare a large enough quantity of the substance to enable a thorough investigation of its properties to be carried out.

Preparation of a Homogeneous Fraction of Alcohol Lignin Chloride

Air-dry spruce sawdust (7 kg.) was chlorinated, as described, in methyl alcohol for a total period of about three weeks, the supernatant layer of alcoholic lignin chloride solution being withdrawn periodically and fresh alcohol being substituted. The crude alcohol lignin chloride was obtained by diluting the alcoholic solution with water. A total yield of 950 gm. (13.5%) of white air-dry product was obtained. This was then suspended in methyl alcohol and subjected to another chlorination period of 10 days, after which most of it had redissolved. The insoluble portion was filtered off and a final yield of about 500 gm. of re-chlorinated product was obtained on precipitation with water. The portion soluble in carbon tetrachloride was then extracted by refluxing the material with successive amounts of carbon tetrachloride until no more lignin dissolved, and the solutions were then united and concentrated by evaporation of the carbon tetrachloride *in vacuo*.

This carbon tetrachloride solution of alcohol lignin chloride was then precipitated, in four fractions, by the gradual addition of petroleum ether. It was found necessary to first dilute it again to about two litres to obtain the familiar creamy white, flocculent precipitate, as otherwise the lignin came down as a brown, scaly resin, similar, evidently to Müller's chlororesin. The fractions were then analyzed for chlorine, with results as shown in Table II.

TABLE II

Fraction No.	Yield, gm.	Color	Chlorine content, %
1	13.2	Cream yellow	43.2
2	38.7	Cream white	35.35, 35.4
3	32.0	Cream white	35.30, 35.4
4	34.2	Cream yellow	37.4

Since Fractions 2 and 3 were of identical chlorine content, it was decided to analyze them further for car-

TABLE III

——	Fraction 2, %	Fraction 3, %
H_2O	6.00	6.65
C	43.01, 43.15	43.7, 43.8, 43.9
	Av. 43.1	Av. 43.8
H	3.40, 3.40	3.47, 3.45 (3.46)
OCH_3	16.95, 16.95	17.96, 17.92

bon and hydrogen to see whether they actually represented a strictly homogeneous fraction of lignin chloride. The complete analyses are given in Table III.

It can be seen that the carbon and hydrogen contents of Fraction 3 are slightly higher than those of Fraction 2, but this can be satisfactorily explained by the higher methoxyl content of Fraction 3. It is clear, from the high methoxyl content of these fractions, that we are dealing with an alcohol lignin, and that evidently more than one of the hydroxyl groups have been methylated by combination with the alcohol during the chlorination. The methoxyl content on a chlorine-free basis would be approximately 26%. Hibbert gives the methoxyl content of his methyl alcohol lignin as 21.45%; that of the mono-methylated product, 24.1%. Hence, it is clear that the lignin chloride has suffered methylation during its isolation and Fraction 3 has been slightly more highly methylated than Fraction 2. A comparison of the two fractions, after allowance is made for this difference in methoxyl, will show them to be virtually identical in composition (Table IV).

TABLE IV

ATOMS PER 100 GM. OF LIGNIN CHLORIDE

——	Fraction 2	Fraction 3	Fraction 3 (corr.)
C	3.56	3.61	3.58
H	3.40	3.46	3.40
Cl	0.997	0.996	0.996
OCH_3	0.547	0.579	0.547

It is seen that there are 0.032 excess methoxyl groups per 100 gm. of lignin in Fraction 3. Since this must have replaced hydroxyl groups, there should be 0.032 atoms of carbon and 0.064 atoms of hydrogen less in Fraction 3, if the two fractions are to be compared on the same methoxyl content basis. The results obtained after making this subtraction are shown in Table IV in the fourth colum, and it is apparent that the two fractions are now of identical composition. Hence, the authors felt justified in proceeding with the investigation of this lignin, since, except for a slight variation in its methoxyl content, it was strictly homogeneous and could be regarded as a definite compound of lignin.

Properties of Alcohol Lignin Chloride

Alcohol lignin chloride is an amorphous, creamy white colored powder, unchanged by heating at 110° C., but which gradually turns brown and melts at 160° to 170° C. and finally carbonizes at about 200° C. It is very soluble in acetone, ethyl acetate, acetic acid, acetaldeyhyde, propionic acid, chloroform, pyridine, quinoline, nitrobenzene, and alcohol plus benzene; completely soluble in 5 to 10% sodium hydroxide, ether plus alcohol, carbon tetrachloride, benzene plus ether, and alcoholic sodium hydroxide; partially soluble in ammonium hydroxide, dilute sodium hydroxide, absolute alcohol, and benzene; insoluble in water, sodium carbonate solution, methyl alcohol, 95% ethyl alcohol, ether, dilute nitric acid, concentrated hydrochloric acid and 50%

sulphuric acid. It has a characteristic varnish-like odor, and is slightly hygroscopic. All experiments were done with the air-dry material and corrected to a bone-dry basis. It is very difficult to dry thoroughly, requiring several days heating *in vacuo* at 80° to 90° C. before attaining a constant weight.

Formula of Alcohol Lignin Chloride

Fraction 2 was used throughout in the experiments described below, and of the various formulas that have been proposed for lignin, that of Hibbert's agrees best with the authors' results. Brauns and Hibbert (2) give as the empirical formula for native lignin, $C_{47}H_{52}O_{16}$, and state that it contains five hydroxyl and five methoxyl groups. In methyl alcohol lignin, one hydroxyl has been replaced by one methoxyl in the extraction process, and in the monomethylated methyl alcohol lignin (methylated with diazomethane) there are accordingly seven methoxyl groups. Fraction 2 seems to be akin to this monomethylated derivative as it also contains seven methoxyl groups, and the differences in the two formulas can be satisfactorily explained by the presence of the chlorine in the authors' preparation. The two formulas are given in Table V, and it will be seen that the authors' analytical and calculated results agree as well, if not better than Hibbert's.

TABLE V

	Fraction 2, alcohol lignin chloride $C_{42}H_{22}O_6Cl_{13}(OH)_2(OCH_3)_7$, mol. wt., 1334		Hibbert's monomethyl alcohol lignin $C_{42}H_{32}O_8(OH)_3(OCH_3)_7$, mol. wt., 900	
	Found, %	Calculated, %	Found, %	Calculated, %
C	43.1	44.1	66.3	65.3
H	3.40	3.37	6.35	6.3
Cl	35.4	34.6	27.35	28.4
O	18.1	18.0	24.9	24.1
OCH_3	16.9	16.3		

It will be noticed that alcohol lignin chloride has 10 hydrogen atoms less than Hibbert's lignin and one hydroxyl group less. These have evidently been replaced by 11 chlorine atoms. There are still two chlorine atoms unaccounted for, which must have entered the molecule to saturate a double bond, as seems probable from the work of Fuchs, Hibbert and Sankey, and Friedrich and Pelikan, who all found lignin capable of addition of bromine.

Methylation of Alcohol Lignin Chloride

Methylation was first attempted with dimethyl sulphate in acetone solution with powdered calcium carbonate added to take up sulphuric acid, since it was feared that sodium hydroxide would split off chlorine from the lignin chloride. However, no further methylation resulted. With pyridine as the solvent, the same negative result was obtained. Sodium hydroxide was finally

used and the experiment carried out according to the procedure of Holmberg and Wintzell (18). The final product after filtering and washing was light brown and was obtained in 50% yield. It was analyzed for methoxyl and chlorine. Found: OCH_3, 19.1; Cl, 19.6%. Although the methoxyl content is higher than the original, this can be seen to be due solely to the loss of chlorine suffered during the methylation. Trial and error showed that the experimental results agreed best with the assumption that seven chlorine atoms had been replaced, and that the methoxyl content had remained unchanged, giving a substance of formula $C_{42}H_{28}O_6Cl_6(OH)_3(OCH_3)_7$. Calcd. for OCH_3, 19.5; Cl, 19.2%. Found: OCH_3, 19.1; Cl, 19.7%. This would mean that six chlorine atoms had been replaced by hydrogen atoms (a result analogous to Powell and Whittaker's findings on chlorinated alkali lignin), and one chlorine atom by a hydroxyl group, probably the same chlorine atom that had replaced a hydroxyl group during the original chlorination.

Acetylation of Lignin Chloride

Since the presence of two hydroxyl groups could not be demonstrated by methylation it was decided to try acetylation, and this proved more successful. Lignin chloride (3 gm.) was dissolved in 35 cc. of acetyl chloride and refluxed for 30 min. (22). The solution was cooled, diluted with acetic acid, and the lignin precipitated by dilution with water. The precipitate was white and seemingly unchanged in appearance. It was filtered, washed free of acid, air-dried, and its moisture content determined. Then the acetyl content was determined by the method of Ost and Katayama (20). In this method the acetyl groups are first hydrolyzed by strong acid or alkali, then the solution is diluted, and the free acetic acid is distilled off in steam, and titrated. Acid hydrolysis failed to yield any appreciable quantity of acetic acid, probably because the lignin would not dissolve in the 50% sulphuric acid used as a hydrolyzing agent. However, by the use of alkaline hydrolysis, a distillate was obtained which required 2.40 cc. of 0.218 *N* sodium hydroxide for an 0.5022 gm. sample of acetylated lignin. The distillate gave no precipitate with silver nitrate and nitric acid. This showed that no chlorine had distilled over. A blank determination run on the original lignin chloride gave a negative result, so it was evident that the lignin chloride had actually been acetylated. The moisture content of the acetylated lignin was 6.3%, so that its acetyl content was:

$$2.40 \times \frac{0.218}{1000} \times \frac{43}{0.5022} \times \frac{100}{93.7} \times 100 = 4.8\% \ .$$

The acetylated lignin was then analyzed for chlorine and methoxyl to make sure that these had not been split off during the acetylation. Found: Cl, 34.3; OCH_3, 15.7%.

The new values calculated on the assumption that the only change in the molecule was an addition of 4.8% of acetyl, *i.e.*, an increase in weight of $\frac{42}{43} \times 4.8 = 4.68\%$ (since one hydrogen atom is replaced by each acetyl

group entering), would be: Cl, $35.4 \times \frac{95.32}{100} = 33.8\%$; OCH_3, $16.9 \times \frac{95.32}{100} = 16.1\%$. These figures agree fairly well with the experimental values and show that neither chlorine nor methoxyl was replaced during the acetylation.

The new molecular weight of this acetylated lignin would be $1334 \times \frac{100}{95.32}$, and the number of acetyl groups which had entered the molecule $= 1334 \times \frac{100}{95.32} \times \frac{4.8}{43} \times \frac{1}{100} = 1.56$.

This figure should be very close to 2.0 if it is to agree with the formula chosen. It was felt that further acetylation might be obtained under different conditions, and experiment proved this to be so. One-half hour acetylation at room temperature gave the greatest value in a series of experiments in which the acetyl content was determined roughly by direct back-titration of the alkali solution used to hydrolyze the acetylated samples. A repeat experiment in which these conditions were used for the acetylation was accordingly performed and the acetyl content of the product was determined as before by steam distillation. The acetic acid in the distillate was determined by titration with 0.105 *N* sodium hydroxide and bromcresol purple as an indicator. A blank was also run on 25 cc. of 0.0105 *N* sodium acetate solution to determine what correction should be applied for the carbon dioxide dissolved in the distillate. The results are given in Table VI.

TABLE VI

Portion	Titrations of distillate from hydrolyzed lignin solution		Titrations of distillate from sodium acetate solution	
	Distillate, cc.	Titre, cc.	Distillate, cc.	Titre, cc.
First	600	2.45	700	2.68
Second	800	0.50	400	0.23
Third	600	0.40	300	0.17
Fourth	800	0.42	800	0.42

Weight of air-dry acetylated product, 0.198 gm.; moisture content, 7.0%.

It is obvious that all the acetic acid comes off in the first two portions of distillate. The titration for the sodium acetate blank should be 2.5 cc., hence the correction on 1100 cc. of distillate is 0.41 cc. (2.91 − 2.50).

Therefore the correction for the first two portions of the distillate from lignin solution (1400 cc.) is 0.52 cc. $\left(\frac{0.41 \times 1400}{1100}\right)$.

The corrected titration is, 2.43 cc. (2.95 − 0.52). Then the percentage of acetyl in the 0.198 gm. sample of acetylated lignin is,

$$\frac{2.43 \times 0.105 \times 43 \times 100 \times 100}{0.198 \times 1000 \times 93} = 5.97 .$$

$$\frac{42}{43} \times 5.97 = 5.82\% = \text{increase in molecular weight.}$$

Hence the number of acetyl groups that have entered the molecule is,

$$\frac{1334}{43} \times \frac{100}{94.18} \times \frac{5.97}{100} = 1.97 \text{ or } 2.0 .$$

This is excellent evidence that the formula chosen for alcohol lignin chloride is correct, since the presence of two hydroxyl groups is confirmed.

Reduction of Alcohol Lignin Chloride

About 10 gm. of lignin was dissolved in 150 cc. of glacial acetic acid and placed in a flask with granulated zinc. Water (20 cc.) was added to facilitate the evolution of hydrogen and the whole left at 40° C. for a week. The solution turned from golden brown to black. The lignin was then recovered by precipitation with water, washed free of acid, and air-dried. Yield, 3 gm. It was still white in color and apparently unchanged. A complete analysis was made; the results are given in Table VII.

It is evident that both chlorine and methoxyl were removed during the reduction, and that at the same time the lignin underwent some acetylation from contact with the acetic acid. The reaction may be represented as:

$$C_{42}H_{22}O_6Cl_{13}(OH)_2(OCH_3)_7 + CH_3COOH + H_2 + H_2O \longrightarrow$$

$$C_{42}H_{28}O_6Cl_6(OH)_4(OCH_3)_5\left(CH_3C\begin{matrix}=O\\ -O\end{matrix}\right) \text{(mol. wt., 1123).}$$

TABLE VII

ANALYSIS OF REDUCED LIGNIN CHLORIDE

	Found, %	Calculated, %
C	51.0	52.3
H	4.46	4.45
Cl	20.1	19.0
OCH_3	13.8	13.8
CH_3CO	3.75	3.83
O	24.3	24.2

Seven chlorine atoms had been removed, six having been replaced by hydrogen atoms and one by a hydroxyl group. This is exactly what happened in the methylation experiment above, so that evidently seven of the chlorine atoms in lignin chloride are readily removed either by alkali or by acid reduction, the other six being firmly bound probably to an aromatic nucleus.

In addition to the removal of chlorine, however, two methoxyl groups have been hydrolyzed off, one being replaced by hydroxyl and the other by acetoxyl, $CH_3C\begin{matrix}\diagup\!\!\!=O\\ \diagdown\!\!\!-O-\end{matrix}$.

The chlorine content is slightly higher than the calculated value for six chlorine atoms. This tends to suggest that the reduction had not gone quite to completion. This was further shown to be the case by fractional precipitation of a sample of the reduced lignin from acetone solution by the gradual addition of alcohol and water. Two fractions were collected and analyzed for chlorine, (1), 19.9; (2), 20.5%. This result showed that the chlorine content was not quite homogeneous throughout the reduced lignin, probably because the reaction had not been allowed to continue long enough to completely remove the seven atoms of chlorine.

Although many other experiments suggested themselves which might have been performed on this chlorinated product of lignin, time did not permit the authors to continue the investigation. However, enough had been done to demonstrate that the body did react stoichiometrically within limits as narrow as could be expected for such a large molecule, and that it confirmed Hibbert's general formula for lignin.

Portion Insoluble in Carbon Tetrachloride

Since more than 200 gm. of the original lignin chloride remained as a residue insoluble in carbon tetrachloride, this portion was separated into three fractions for the use of future investigators, and one fraction was completely analyzed as a matter of interest to see how its constitution compared with that of the portion soluble in carbon tetrachloride.

The product was dissolved in acetone, and a fraction precipitated by the addition of carbon tetrachloride. This fraction came down as a brownish resin, and it was filtered off and dried. Yield, 74 gm. of an orange brown, brittle, resinous-looking material. A second fraction (1*A*) was obtained by the addition of more carbon tetrachloride to the original solution, and a third fraction (1*B*) was precipitated by the addition of petroleum ether to the mother liquor. 1*A* was yellowish white in color (Cl, 34.5%; yield, 44 gm.); 1*B* was cream white in color (Cl, 32.0%; yield, 84 gm.). Fraction 1*B* was then analyzed completely, and was also tested for homogeneity. A portion was dissolved in acetone, and, by the gradual addition of carbon tetrachloride and petroleum ether, three fractions were precipitated successively. Upon analysis these gave the following chlorine contents: (i) 31.2, (ii) 32.3, (iii) 32.7%; accordingly Fraction 1*B* was not strictly homogeneous.

TABLE VIII

ANALYSIS OF FRACTION 1*B*

	Found, %	Calculated, %
C	49.4	48.0
H	3.56	3.58
O	16.0	15.0
Cl	32.0	32.5
OCH_3	15.4	15.5

However, its analysis gives a clue to its average constitution, and shows its relation to the fraction soluble in carbon tetrachloride (Fraction 2, Table V).

The average constitution of Fraction 1*B* is represented fairly accurately by the empirical formula $C_{48}H_{43}O_{12}Cl_{11}$.

The formulas of Fractions 1*B* and 2, Table V, may now be compared along with Hibbert's formula for native lignin:

Hibbert's native lignin—$C_{42}H_{32}O_6(OH)_5(OCH_3)_5$
Fraction (2) —$C_{42}H_{22}O_6Cl_{13}(OH)_2(OCH_3)_7$
Fraction 1*B* —$C_{42}H_{25}O_6Cl_{11}(OCH_3)_6$.

It is seen that Fraction 1*B* is quite different from No. 2. Only one hydroxyl group has been methylated during the chlorination and just 11 chlorine atoms have entered the molecule. Seven of these chlorine atoms have evidently replaced seven hydrogen atoms, and the other four have gone to replace the remaining four hydroxyl groups, leaving the product free of hydroxyl groups. The future investigation of this body should accordingly prove very interesting.

References

1. Beamish, F. E. Ind. Eng. Chem., Anal. Ed. 6 : 352-353. 1934.
2. Brauns, F. and Hibbert, H. Pulp Paper Mag. Can. 34 : 187-188. 1933.
3. Cross, C. F. and Bevan, E. J. Chem News, 42 : 91. 1880.
4. Cross, E. F. and Bevan, E. J. J. Chem. Soc. 43 : 18-21. 1883.
5. Cross, E. F. and Bevan, E. J. Cellulose. Longmans, Green and Company, London. 1918.
6. Friedrich, A. and Brüda, B. Monatsch. 46 : 597-610. 1925.
7. Friedrich, A. and Diwald, J. Monatsch. 46 : 31-46. 1925.
8. Friedrich, A. and Pelikan, E. Biochem. Z. 239 : 461-472. 1931.
9. Fuchs, W. Brennstoff-Chem. 9 : 348-350. 1928.
10. Fuchs, W. Brennstoff-Chem. 9 : 363-365. 1928.
11. Fuchs, W. and Horn, O. Ber. 61, B : 2197-2202. 1928.
12. Hägglund, E. and Rosenquist, T. Biochem. Z. 179 : 376-383. 1926.
13. Heuser, E. and Ackermann, W. Cellulosechem, 5 : 13-21. 1924.
14. Heuser, E. and Casseus, H. Papierfabr. Fest-Auslandheft, 80-93. 1922.
15. Heuser, E. and Sieber, R. Z. angew. Chem. 26 : 801-806. 1913.
16. Hibbert, H. and Sankey, C. A. Can. J. Research, 4 : 110-118. 1931.
17. Hibbert, H. and Taylor, K. A. Can. J. Research, 4 : 240-253. 1931.
18. Holmberg, B. and Wintzell, T. Ber. 54 : 2417-2425. 1921.
19. Müller, O. A. Papier-Fabr. 32 : 329-332, 338-342, 347-351, 354-358. 1934.
20. Ost, H. and Katayama, T. Z. angew. Chem. 25 : 1467-1470. 1912.
21. Paschke, F. Cellulosechemie, 3 : 19-21. 1922.
22. Powell, W. J. and Whittaker, H. J. Chem. Soc. 125 : 357-364. 1924.
23. Powell, W. J. and Whittaker, H. J. Chem. Soc. 127 : 132-137. 1925.
24. Rassow, B. and Zickmann, P. J. prakt. Chem. 123 : 189-234. 1929.
25. Taylor, K. A., Maass, O. and Hibbert, H. Can. J. Research, 4 : 119-133. 1931.
26. Waentig, P. Z. angew. Chem. 41 : 493-498, 977-980, 1001-1005. 1928.

FREE RADICALS IN ORGANIC DECOMPOSITION REACTIONS

I. THE THERMAL DECOMPOSITION OF MIXTURES OF METHYL ETHER AND DEUTERO-ACETONE[1]

By E. W. R. Steacie[2] and W. A. Alexander[3]

Abstract

A new method of obtaining information concerning the participation of free radicals in decomposition reactions is described. A mixture of two organic compounds is decomposed, all the hydrogen in one of the compounds having been replaced by deuterium. By an examination of the distribution of deuterium among the products, it is possible to obtain considerable insight into the mechanism of the process.

Mixtures of deutero-acetone and dimethyl ether have been decomposed at 590° C. It is found that the hydrogen in the products is entirely "light" within the experimental error. This precludes the possibility that formaldehyde (which is the source of the hydrogen) decomposes by a free radical mechanism, HCHO = H + CHO, as otherwise reaction of hydrogen atoms with deutero-acetone would lead to the formation of HD.

It is also concluded that it is unlikely that formaldehyde formed in the methyl ether decomposition is decomposed by sensitization from methyl radicals from the ether decomposition. If this were the case we would expect to have the reactions

$$\begin{aligned} CH_3 + HCHO &= CH_4 + CHO \\ CHO &= CO + H, \end{aligned}$$

and again hydrogen atoms by reaction with deutero-acetone would yield HD.

The method of investigation seems to have interesting possibilities and to be of wide applicability.

Introduction

There is at present considerable uncertainty regarding the importance of free radicals in organic decomposition reactions. Information on this point is particularly desirable in the case of substances which decompose by a first order mechanism, in view of the suggestion of Rice and Herzfeld (18) that practically all first order reactions might really be chain processes involving atoms and radicals.

Experimental information on this point is available from various sources. The work of Rice and his collaborators, following up the original discovery of Paneth and Hofeditz (14), has definitely established the production of free radicals in large quantities when various organic compounds are heated to temperatures between 800° and 1000° C. (20). Rice and Herzfeld showed that it was possible to construct reasonable mechanisms on a free radical chain basis which would lead to agreement with the observed kinetics of decomposition reactions.

Striking support for the Rice-Herzfeld mechanisms was immediately forthcoming. Frey (6) was able to start chains in *n*-butane at temperatures below its normal decomposition range by adding methyl radicals produced by the decomposition of dimethyl mercury. Similarly Allen and Sickman (2, 23) were able to initiate chain decomposition in acetaldehyde with methyl

[1] *Manuscript received June 1, 1937.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada, with financial assistance from the National Research Council of Canada.
[2] *Assistant Professor of Chemistry, McGill University.*
[3] *Holder of a bursary under the National Research Council of Canada.*

radicals from the decomposition of azomethane. Leermakers (13) also produced sensitized chain decomposition of methyl ether at temperatures below 400° C. by photolyzing admixed acetone. All these researches prove that radicals *can* cause chain decomposition of a large number of organic substances. They do not, however, necessarily prove that such free radical chains occur in the normal pyrolysis of the substances concerned.

Further evidence for the chain character of a number of decomposition reactions is furnished by the work of Staveley and Hinshelwood (24, 25, 26). They found that while large amounts of nitric oxide will catalyze numerous reactions, small amounts cause some inhibition. They assume that the maximum inhibition corresponds to a complete suppression of chains normally present, and thus calculate chain lengths of from two to four for the decomposition of diethyl ether, propionaldehyde, and ethyl propyl ether. If their conclusions are correct this is evidence for chains, but is definitely evidence against the Rice-Herzfeld scheme, since the chain lengths found experimentally are far too small. However, the assumption that maximum inhibition corresponds to a complete suppression of all chains is extremely arbitrary, and makes the calculated chain lengths of little real significance.

On the other hand, rather definite evidence against the radical chain theory is furnished by the work of Patat and Sachsse (15, 16, 17, 22). They measured the rate of the ortho-para hydrogen conversion in the presence of decomposing organic compounds, and were thus able to detect hydrogen atoms produced by the decomposition or by the reaction

$$CH_3 + H_2 = CH_4 + H \ . \qquad (A)$$

In general, the hydrogen atoms produced in this way are being destroyed by the reaction

$$H + RH = H_2 + R \ , \qquad (B)$$

where RH is an organic molecule and R a free radical. Hence the stationary concentration of hydrogen atoms is defined by the two processes and we get approximately

$$(CH_3)/(H) = k_B(RH)/k_A(H_2) \ .$$

Having evaluated the hydrogen atom concentration by means of the rate of the ortho-para hydrogen conversion, we can thus calculate the concentration of methyl radicals and compare it with the value calculated from the Rice-Herzfeld mechanism. In general, using the activation energies assigned to the above reactions by Rice and Herzfeld, Patat and Sachsse find the hydrogen atom concentrations to be lower, by several powers of 10, than those calculated from the free radical chain theory.

Another way of testing the theory is to determine in an independent way the activation energies of one or more of the part reactions in the Rice-Herzfeld mechanism for a given substance, and compare them with those assigned in order to obtain agreement with experiment for the over-all reaction.

In the case of the ethane decomposition, for example, one of the fundamental steps in the free radical mechanism is (18)

$$H + C_2H_6 = H_2 + C_2H_5 . \qquad E = 17 \text{ Kcal.}$$

Steacie and Phillips (28) investigated this reaction by the atomic deuterium method and estimated the activation energy to be 6.3 Kcal. If we use this value instead of 17 Kcal., the Rice-Herzfeld mechanism no longer predicts the correct order or over-all activation energy for the ethane decomposition.

It follows from the above discussion that the existing experimental evidence concerning the participation of free radicals in organic decomposition reactions is inconclusive and somewhat conflicting. It is therefore desirable to search for other methods of investigation which may throw some light on the problem. With this end in view, experiments have been carried out in which a mixture of two organic compounds is decomposed. In one of these compounds all the hydrogen atoms have been replaced by deuterium. If decomposition occurs by a molecular mechanism, the products of the decomposition of one compound should be entirely "heavy," while those of the other are entirely "light." If, however, free radicals or atoms intervene, then cross-products will be formed. It is therefore possible to obtain considerable information concerning the mechanism of the decomposition from an examination of the distribution of deuterium among the products. The present communication describes experiments of this sort with mixtures of dimethyl ether and deutero-acetone.

It is known that the products formed in the decomposition of these two substances are mainly those indicated by the equations:

$$\begin{aligned} CH_3OCH_3 &= CH_4 + HCHO \\ &= CH_4 + H_2 + CO \text{ (10)}, \\ CH_3COCH_3 &= CH_4 + CH_2{=}CO \\ &= CH_4 + CO + \tfrac{1}{2} C_2H_4 \text{ (11, 21, 30, 31)} . \end{aligned}$$

The decomposition of acetone is not as smooth as that of methyl ether, and the products are not in exact agreement with the above equation. However, the important thing for our purpose is that very little hydrogen is formed (about 2%). Hence, virtually all the hydrogen formed in the pyrolysis of a mixture of methyl ether and acetone arises from the methyl ether.

If, therefore, the reactions proceed by a molecular mechanism, we should expect on decomposing a mixture of methyl ether and deutero-acetone to find that the resulting hydrogen was almost entirely "light." On the other hand, if the formaldehyde from the ether decomposition itself decomposes by a free radical mechanism, we should have (15)

$$\begin{aligned} HCHO &= H + CHO \\ CHO &= CO + H \\ H + HCHO &= H_2 + CHO \end{aligned}$$

etc.,

a reaction chain being set up. In the presence of deutero-acetone, however, the reaction

$$H + CD_3COCD_3 = HD + CD_2COCD_3$$

can also occur, and the hydrogen in the products should be deuterized to a considerable extent. We can thus determine whether or not free hydrogen atoms have appeared during the decomposition process by analyzing the hydrogen formed.

It should be mentioned that at the temperature employed in this work (590° C.) methyl ether decomposes about five times faster than acetone. Hence, when formaldehyde is decomposing there will always be available ample acetone to react with any hydrogen atoms which may be formed.

Experimental

Apparatus

The apparatus is illustrated in Fig. 1. The pumping system (not shown) was of the usual type, consisting of a rotary oil pump, a mercury vapor pump, and liquid air traps. The left-hand section of the apparatus, consisting of

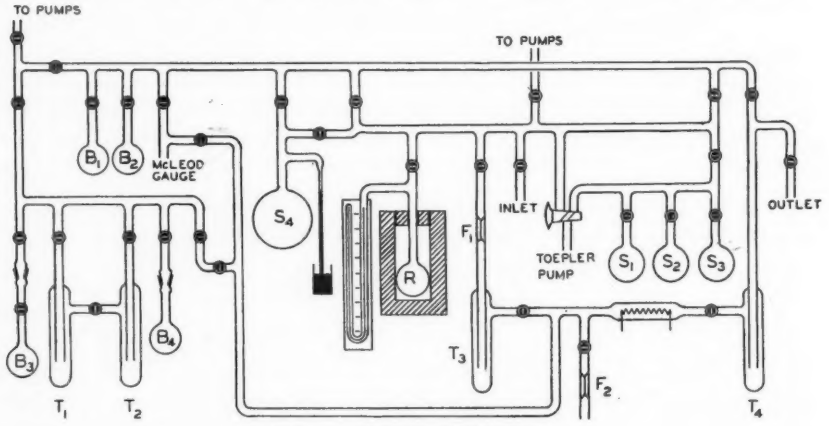


FIG. 1. *Diagram of apparatus.*

bulbs B_1, B_2, B_3, and B_4, and traps T_1 and T_2, was used for the preparation, distillation, and storage of deutero-acetone, as described later. Dimethyl ether was introduced into the apparatus through the tube marked "Inlet" and was stored in bulb S_1. Mixtures of acetone and ether were made up and stored in S_4. The reactants were decomposed in the fused silica reaction vessel, R, of 500 cc. capacity. This was connected to the apparatus and to a capillary manometer through a quartz to soft glass graded seal. The manometer and connecting tubing attached to the reaction vessel were wound with nichrome wire and electrically heated to prevent condensation. The reaction vessel was surrounded by an electric furnace, the temperature of which was controlled by hand regulation of rheostats. Temperatures were measured by means of a chromel-alumel thermocouple in conjunction with a

Cambridge thermocouple potentiometer. The temperature could be maintained constant to within ± 2°. All runs were made at 590° C. and with a 1:1 mixture of ether and acetone. The initial pressure of the reaction mixture was approximately 20 cm. throughout.

After the reaction had proceeded for the desired time, the reaction products were transferred by means of a Toepler pump to the storage bulbs S_2 and S_3. In order to obtain sufficient products for analysis, it was necessary to make several decompositions under identical conditions and combine the products in the storage bulbs.

The Separation of the Products

The next step in the procedure was to separate the hydrogen from the other products in order to determine its deuterium content. This was accomplished by letting the products in the reservoir S_2 or S_3 flow slowly through the capillary flowmeter F_1 and then through the trap T_3 filled with silica gel and maintained at −180° C. All the products but hydrogen and some carbon monoxide are removed by this procedure (8). Dry oxygen was metered in at F_2, and the H_2–CO–O_2 mixture was burned on the electrically heated platinum spiral. The resulting water was collected in the cold trap T_4. At the completion of the separation, the water in T_4 was distilled into a bulb attached to the "Outlet" by a ground joint, and was then transferred to a deuterium analysis apparatus.

Deuterium Analysis

The water obtained as above was distilled thoroughly *in vacuo* to remove dissolved carbon dioxide, or other gases, and was then analyzed for its deuterium content by determining the heat conductivity of the saturated vapor at −21° C. as described in previous papers (7, 8).

Materials

Methyl ether was obtained in cylinders from the Ohio Chemical and Manufacturing Co., and was fractionally distilled before use.

Deutero-acetone was prepared by exchange with deuterium oxide in slightly alkaline solution by the method of Halford, Anderson, Bates, and Swisher (9). Potassium carbonate (0.04 gm.), 99.6% deuterium oxide (10 gm.), and pure acetone (10 gm.) were heated to 43° to 45° C. for about 24 hr. The water and acetone were distilled onto pure anhydrous calcium chloride, and the acetone was rapidly distilled off to a trap kept at −78° C. The calcium chloride was dehydrated by warming to 70° C. and evacuating for about an hour, and the distillation was repeated to remove the remaining traces of water. Analysis showed the product to be 38.8% deuterized. Almost all of this material was used up in trial runs. In preparing a second sample, with which almost all the runs which are reported here were made, light acetone was first "exchanged" with the deuterium oxide residue from the first preparation, and then retreated with 99.6% deuterium oxide. This gave a product which was 48.3% deuterized.

Results

It should be emphasized at the outset that the present work is of a preliminary nature. The experimental technique is difficult since it involves the separation of a small amount of one product from a complex mixture, and its analysis for deuterium on a micro scale. As a result the greatest accuracy to be expected in the deuterium content in the present work is about ± 2%.

Throughout the present investigation equimolecular mixtures of methyl ether and deutero-acetone were used. Since both molecules contain the same number of hydrogen atoms, complete exchange would yield the following deuterium contents (if it is assumed that the distribution coefficient is unity):

Acetone sample	% D in acetone	% D in hydrogen from the decomposition if exchange were complete
I	38.8	19.4
II	48.3	24.2

However, as discussed above, a free radical mechanism would probably involve as the main steps:

$$HCHO = H + CHO \quad (1)$$

$$CHO = H + CO \quad (2)$$

$$H + CD_3COCD_3 = HD + CD_2COCD_3 \quad (3)$$

$$H + CH_3OCH_3 = H_2 + CH_2OCH_3. \quad (4)$$

If Reactions (3) and (4) are equally likely, it follows that we would at the most expect the hydrogen to be 25% exchanged, *i.e.*, we would expect the deuterium content of the hydrogen to be 9.7% for acetone Sample I, and 12.1% for Sample II.

It is obviously necessary in the first instance to test the efficiency of the separation of the gases, and to prove the absence of appreciable amounts of hydrogen from the acetone decomposition. This was accomplished by making blank runs in which methyl ether and deutero-acetone were decomposed separately, the products mixed at room temperature, and the hydrogen separated, burned, and analyzed. The results of such runs are given in Table I.

TABLE I

BLANK RUNS TO TEST THE EFFICIENCY OF SEPARATION OF HYDROGEN FROM THE OTHER PRODUCTS. REACTANTS DECOMPOSED SEPARATELY, MIXED, AND THE HYDROGEN SEPARATED, BURNED, AND ANALYZED

Run No.	Acetone sample	% D in hydrogen
2	I	0.0
3	I	1.3
5	II	2.0
6	II	2.0
		Mean 1.3

The mean deuterium content thus found is no greater than that to be expected from the small amount of deuterium formed in the acetone decomposition, and the method of separation of the products may therefore be considered satisfactory.

There is, however, another point which must be tested. Suppose that the two substances decompose entirely independently to give H_2, CH_4, CD_4, C_2D_4, CO, etc. It is still possible that an exchange reaction might occur at the high temperature used, of the type

$$H_2 + CD_4 = HD + CHD_3, \qquad (5)$$

or

$$H_2 + C_2D_4 = HD + C_2D_3H \qquad (6)$$
$$\text{or} = D_2 + C_2D_2H_2.$$

Of these, Reaction 5 is known to be negligibly slow at 590° C. (3, 27). There is, however, considerable likelihood of Reaction (6) occurring via the ethane equilibrium, viz.

$$H_2 + C_2D_4 = C_2D_4H_2 = C_2D_4 + H_2$$
$$\text{or} = C_2D_2H_2 + D_2$$
$$\text{or} = C_2D_3H + HD.$$

To test this possibility, runs were made in which deutero-acetone and methyl ether were decomposed separately, and the products were then mixed and heated together for a definite time at 590° C. The results of such experiments are given in Table II.

TABLE II

BLANK EXPERIMENTS TO TEST THE POSSIBILITY OF AN EXCHANGE REACTION BETWEEN THE PRODUCTS

Run No.	Acetone sample	Heating time, min.	% D in hydrogen
9	II	32	11.8
10	II	5	0.0
12	II	5	6.4
14	II	5	0.0
16	II	5	1.5
18	II	5	6.9
		5	Mean 3.0

It is apparent from the table that with long periods of heating the exchange reaction becomes troublesome. In fact with 32 min. heating time the exchange has proceeded about halfway to equilibrium. On the other hand, the mean deuterium content of the hydrogen after five minutes heating time is only 3.0%, as compared with 1.3% for the blank runs given in Table I. Hence, with this time of heating the exchange is not serious. It should, therefore, be safe to draw conclusions from experiments in which mixtures of methyl ether and acetone are heated together at 590° C. for not more than five minutes. It may be mentioned that this time is sufficient to effect the complete decomposition of methyl ether, and to decompose about 90% of the acetone.

The results of experiments with mixtures of the two substances are given in Table III.

A comparison of Tables II and III shows that there is no appreciable increase in the deuterium content of the hydrogen during the decomposition of the mixture. It may therefore be concluded that free hydrogen atoms have not made their appearance to any considerable extent during the process. The results in Tables II and III show considerable fluctuations, which sharply limit the attainable accuracy. The experiments were carried out in pairs, *i.e.*, Runs 10 and 11, 12 and 13, etc., were done in succession and the products analyzed at the same time. It is apparent that the fluctuations usually affected both members of a pair, thus Runs 12, 13, and 18, 19 all gave high results. It is possible that these variations are to be associated with changes in surface activity. It is hoped to obtain more information on this point in further work with improved analytical methods.

TABLE III

DECOMPOSITION OF MIXTURES OF METHYL ETHER AND DEUTERO-ACETONE AT 590° C.

Run No.	Acetone sample	Reaction time, min.	% D in hydrogen
1	I	32	12.8
7	II	32	15.8
8	II	32	11.4
11	II	5	2.0
13	II	5	5.9
15	II	5	2.0
17	II	5	3.9
19	II	5	5.5
		5	Mean 3.9

Discussion

Within the experimental accuracy it may definitely be concluded that there is no noticeable occurrence of the reaction

$$H + CD_3COCD_3 = HD + CD_2COCD_3.$$

There are obviously two possible causes of the absence of this reaction:

(*a*) No hydrogen atoms are present during the decomposition process.

(*b*) Hydrogen atoms are present, but the reaction has too high an activation energy to proceed at a measurable rate. In other words, its activation energy is much higher than those of other hydrogen atom consuming reactions, such as

$$H + HCHO = H_2 + CHO,$$

and

$$H + CH_3OCH_3 = H_2 + CH_2OCH_3.$$

The evidence seems to be definitely against the second explanation. Methyl ether and acetone are molecules of similar complexity, and there is no reason to assume any appreciable difference in the strength of the carbon-hydrogen

bond or in the steric factor (13). Rice (18, 20) assumes the same activation energy for the reactions

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3$$

and

$$CH_3 + CH_3OCH_3 = CH_4 + CH_2OCH_3.$$

If this is so, there is no reason to expect the hydrogen atom reactions to be very different. As a matter of fact Rice's method of estimating the activation energies of such reactions (20) leads to the conclusion that the reactions of hydrogen atoms with acetone should be faster than the reaction with methyl ether.

It is true that methyl radicals can start a chain decomposition of methyl ether at 400° C., while they cannot do so with acetone (5, 13, 19), and this might be taken as evidence that reactions of the type

$$R + CH_3COCH_3 = RH + CH_2COCH_3$$

do not occur readily. However, although there is evidence against a chain decomposition of acetone (24, 25, 26), there is also ample evidence that radicals will react with acetone (19). (As a matter of fact there is also some evidence that acetone may decompose by a chain mechanism (1, 12)). It has also been observed (4, 5) that acetone can inhibit the radical sensitized decomposition of acetaldehyde by removing radicals from the system. Hence, while chains are apparently not easy to start in acetone, radicals react with it readily, and there seems to be no reason to doubt that the reaction

$$H + CH_3COCH_3 = H_2 + CH_2COCH_3$$

can occur readily at 590° C.

Inasmuch as formaldehyde is present only in small amount, it cannot compete seriously with acetone as a hydrogen atom consuming substance.

We seem therefore to be reduced to the first alternative, *viz.*, that practically no hydrogen atoms are formed in the decomposition processes. This is not in conflict with previous conclusions that radicals may participate in the decomposition of methyl ether (4, 13, 24, 25, 26), since the main steps in the postulated free radical mechanism for the methyl ether decomposition do not involve hydrogen atoms, *viz.*

$$\begin{aligned} CH_3OCH_3 &= CH_3 + CH_3O \\ CH_3 + CH_3OCH_3 &= CH_4 + CH_2OCH_3 \\ CH_2OCH_3 &= CH_3 + HCHO \end{aligned}$$

Our results, however, make it very unlikely that formaldehyde can decompose by a free radical mechanism such as

$$\left.\begin{aligned} HCHO &= CHO + H \\ CHO &= CO + H \\ H + HCHO &= H_2 + CHO \\ 2\,H &= H_2 \end{aligned}\right\}\text{chain}$$

$$2\,CHO = HCHO + CO.$$

This is in agreement with the conclusions of Patat and Sachsse (15) who found a negligibly small stationary hydrogen atom concentration during the thermal decomposition of formaldehyde.

Fletcher and Rollefson (4) have pointed out that formaldehyde formed as an intermediate in the decomposition of methyl ether itself decomposes about 15 times faster than normal. They suggest that this is due to a sensitized decomposition by methyl radicals from the ether decomposition, *viz.*

$$CH_3 + HCHO = CH_4 + CHO$$
$$CHO = CO + H.$$

Since this would also involve the occurrence of free hydrogen atoms, our experiments are not in agreement with such a mechanism.

References

1. Allen, A. O. J. Am. Chem. Soc. 58: 1052-1053. 1936.
2. Allen, A. O. and Sickman, D. V. J. Am. Chem. Soc., 56: 2031-2034. 1934.
3. Farkas, A. J. Chem. Soc. 26-36. 1936.
4. Fletcher, C. J. M. and Rollefson, G. K. J. Am. Chem. Soc. 58: 2129-2135. 1936.
5. Fletcher, C. J. M. and Rollefson, G. K. J. Am. Chem. Soc. 58: 2135-2140. 1936.
6. Frey, F. E. Ind. Eng. Chem. 26 : 200. 1934.
7. Geib, K. H. and Steacie, E. W. R. Trans. Roy. Soc. Can. III, 29 : 91-103. 1935.
8. Geib, K. H. and Steacie, E. W. R. Z. physik. Chem. B29 : 215-224. 1935.
9. Halford, J. O., Anderson, L. C., Bates, J. R. and Swisher, R. D. J. Am. Chem. Soc. 57 : 1663-1665. 1935.
10. Hinshelwood, C. N. and Askey, P. J. Proc. Roy. Soc. (London), A115 : 215-226. 1927.
11. Hinshelwood, C. N. and Hutchison, W. K. Proc. Roy. Soc. (London), A111 : 245-257. 1926.
12. Huffman, J. R. J. Am. Chem. Soc. 58 : 1815-1816. 1936.
13. Leermakers, J. A. J. Am. Chem. Soc. 56 : 1899-1904. 1934.
14. Paneth, F. and Hofeditz, W. Ber. 62B : 1335-1347. 1929.
15. Patat, F. and Sachsse, H. Nach. Ges. Wiss. Göttingen, III, 1 : 41-48. 1935.
16. Patat, F. and Sachsse, H. Z. physik. Chem. B31 : 105-124. 1935.
17. Patat, F. and Sachsse, H. Naturwiss. 23 : 247. 1935.
18. Rice, F. O. and Herzfeld, K. F. J. Am. Chem. Soc. 56 : 284-289. 1934.
19. Rice, F. O., Radowskas, E. L. and Lewis, W. R. J. Am. Chem. Soc. 56 : 2497-2498. 1934.
20. Rice, F. O. and Rice, K. K. The aliphatic free radicals. Johns Hopkins Press, Baltimore. 1935.
21. Rice, F. O. and Vollrath, R. E. Proc. Nat. Acad. Sci. (Washington) 15 : 702-705. 1929.
22. Sachsse, H. and Patat, F. Z. Elektrochem. 41 : 493-494. 1935.
23. Sickman, D. V. and Allen, A. O. J. Am. Chem. Soc. 56 : 1251. 1934.
24. Staveley, L. A. K. and Hinshelwood, C. N. Nature, 137 : 29. 1936.
25. Staveley, L. A. K. and Hinshelwood, C. N. J. Chem Soc. (London), 812-818. 1936.
26. Staveley, L. A. K. and Hinshelwood, C. N. Proc. Roy Soc. (London) A154 : 335-348. 1936.
27. Steacie, E. W. R. Can. J. Research, B, 15 : 264-273. 1937.
28. Steacie, E. W. R. and Phillips, N. W. F. J. Chem. Phys. 4 : 461-468. 1936.
29. Steacie, E. W. R. and Phillips, N. W. F. J. Chem. Phys. 5 : 275. 1937.
30. Williamson, A. T. J. Am. Chem. Soc. 56 : 2216-2218. 1934.
31. Winkler, C. A. and Hinshelwood, C. N. Proc. Roy. Soc. (London), A149 : 340-354. 1935.

THE OCCURRENCE OF "MOTTLED ENAMEL" OF TEETH IN ALBERTA AND ITS RELATION TO THE FLUORINE CONTENT OF THE WATER SUPPLY[1]

By Osman James Walker[2] and Elvins Yuill Spencer[3]

Abstract

A partial survey of the Province of Alberta shows that mottled enamel of the teeth in a mild form is endemic in several parts of the province, especially in the area surrounding Lethbridge and in the area south of Red Deer. From an examination of more than 250 samples of water from different parts of the province, a relation has been found to exist between high fluorine in the water supply and the prevalence of mottled enamel.

A great deal of information on the occurrence of the tooth defect known as mottled enamel has been collected since it was described by Black (3) and McKay (15–18). Surveys have shown that it is endemic in many parts of the United States (9), in parts of Europe, Asia, South America, and South Africa. Early investigations proved that the prevalence of this malady was in some way related to the water supply of the region, that the attack on the teeth took place while the permanent teeth were forming, and that the defect persisted throughout the life of the individual. In 1931, Smith, Lantz and Smith (21, 22) produced evidence to prove that mottled enamel is caused by fluorides in the water supply. Churchill (6) arrived at the same conclusion at nearly the same time. Smith and her colleagues were able to show that concentrations of fluorine greater than 1 p.p.m.* induced mottled enamel in young rats, the intensity of the attack increasing with increasing concentrations of fluorine. In regions in which the mottling was endemic the severity of the defect produced on the teeth of humans varied with the fluorine content of the water. As a result of their investigations and those carried out later, it would seem that fluorine is nearly always present in detectable quantities in natural waters, but that at least 1 p.p.m. (17) is necessary to cause the milder form of mottling, which consists of the formation of opaque white spots or bands usually on the upper teeth. The severity of attack and also the depth of color—white, yellow, brown, black—increases as the fluorine content of the water rises to 2 or 4 p.p.m., or more. When the amount present is more than 12 p.p.m. bones are apparently attacked (14).

When the relation between mottled enamel and the fluorine content of water was established, a great deal of interest was shown in the development of methods for determining minute amounts of fluorine. During the last five years many articles on this subject have appeared. Many of the new methods depend upon the fact that zirconium compounds form a red colored lake with sodium alizarinsulphonate, which, in the presence of fluoride, fades in

[1] *Manuscript received May 4, 1937.*
Contribution from the Department of Chemistry, University of Alberta, Edmonton, Canada.
[2] *Professor of Chemistry, University of Alberta.*
[3] *Final year Honours Chemistry student, University of Alberta.*
* *p.p.m. = Parts per million parts of water.*

proportion to the amount of fluoride present (5, 8, 16). This reaction leads directly to a colorimetric method. A volumetric method (1, 2, 4, 24) is based on later removing the fluoride from solution by titration with a standard solution of thorium nitrate; in this way the lake is allowed to form. Others (10, 11, 12, 23) make use of the fact that fluorides when added to a known amount of ferric ion produce the ferri-fluoride ion, FeF_6^{-3}, so that when thiocyanate is added, the color formed is due to the excess of ferric ion. The spectrograph (6) has also been used. Much of the work in perfecting methods of analysis has been done because of the tendency of other ions to interfere, so that modifications have had to be made. One might say that at the present time methods of determining small amounts of fluorine are fairly satisfactory, although the different methods do give slightly different results.

In the discussions on mottled enamel which appear in the various scientific journals there is no mention of its occurrence in Canada. It is the purpose of this paper to present evidence that there are, in Alberta, several districts where the teeth of many of the children show marked signs of mottling, but, in most cases, of the opaque white, or mild, variety, although several sets of teeth have been examined on which the spots were yellow or light brown. The first evidence came in July, 1935, from Granum in Southern Alberta when the principal of the school described to one of the writers the peculiar appearance of the teeth of some of the children. It was suggested that the trouble was mottled enamel. Clinical evidence from the local dentist was requested and arrangements were made to obtain samples of water from wells in the district. Later, it was learned that the Provincial Travelling Clinic had observed 14 cases at its Grassy Lake centre, the children coming from three different schools. Samples of water were requested from families in these districts. When the University session opened, students coming from several other districts were noticed who had mottled enamel.

Because of these facts, a survey was begun in which as much data as possible were collected and, at the same time, samples of water from many points were obtained and analyzed for fluorine content. Questionnaires were sent to dentists and doctors in the affected areas and co-operation was obtained from the Provincial Department of Health. Students were asked to bring in samples of water, and to report as much evidence of teeth disfigurement as possible. Samples of water received by the Provincial Analyst from different parts of the province were also examined for fluorine content. The teeth of all new students entering the University in the fall of 1936 were examined for this defect by a dentist.

The information received on the prevalence of mottled enamel is not nearly as complete as had been expected. Efforts have been made to obtain as complete a case history of the people as possible, and only those have been included who have lived in the one district between the ages of two and twelve years. It has been rather difficult to ascertain when a family has abandoned one well and begun to use another, and the water supply in many districts comes from both deep and shallow wells in which fluorine content varies

over a wide range. Another difficulty that has been encountered in the survey is the sparseness of settlement and the scarcity of dentists. In addition, the mottled enamel is, of itself, not always sufficient cause for a visit to the dentist.

As the methods for the determination of minute quantities of fluorine are all very recent, it was found necessary to check up on a number of them in order to select the ones that best suited the conditions, and to modify them wherever necessary. After a considerable amount of work had been done it was decided to use; *(a)* a modification of Sanchis' method (19) for amounts of fluorine between 0 and 0.75 p.p.m.; *(b)* Sanchis' regular method for amounts between 0.75 and 3 p.p.m.; and *(c)* a revision of Armstrong's modification (1) of Boruff and Abbot's distillation method (4), which is based on the macro method of Willard and Winter (24), for amounts greater than 2 p.p.m.

In all cases the Sanchis method and the modified Sanchis method were first used, and if the sample contained more than 2 p.p.m. of fluorine, the modified method of Armstrong was used and thus an overlapping was obtained. The first two methods are colorimetric in character and require 100 cc. of water, while the last method is titrimetric, the amount of water required depending on the concentration of fluorine in the water.

Details of the Sanchis method will be found in the original article. It consists essentially of forming the red lake of sodium alizarinsulphonate or alizarin red with a zirconium salt. The color changes on addition of fluoride progressively to a yellow due to the formation of one of the zirconium fluoride (13) complexes, $Zr_3F_{17}^{-5}$, $Zr_2F_{13}^{-5}$, ZrF_5^{-1}, ZrF_6^{-2} or ZrF_7^{-3}, which causes the decomposition of the lake. The reactions are carried out in the presence of large excess of hydrochloric and sulphuric acids to minimize the effect of interfering anions in the natural waters. The colors developed in the solutions containing fluorides were compared with those of standards made up from definite amounts of fluorine, as sodium fluoride, treated in the same manner.

In the modified Sanchis method, to 100 cc. of the water were added 2.0 cc. of 3 *N* hydrochloric acid, 2.0 cc. of 3 *N* sulphuric acid and 1.75 cc. of the indicator containing 0.17 mg. of sodium alizarinsulphonate and 0.87 mg. of c.p. zirconium nitrate, $ZrO(NO_3)_2 \cdot 2H_2O$, per cc. The solution was heated to boiling, allowed to stand for four hours, transferred to a Nessler tube, and the color was matched with solutions containing known amounts of sodium fluoride treated in the same manner.

For the modified Armstrong method the amount of water used was such that approximately 0.2 mg. of fluorine was present. This was made alkaline to phenolphthalein with 0.2 *N* sodium hydroxide and concentrated to 50 cc. This was then placed in a 250 cc. distilling flask along with 20 cc. of concentrated sulphuric acid and some glass beads. The flask was fitted with a thermometer extending into the liquid and a dropping funnel connected to a capillary tube also extending into the liquid so that water could be added from time to time. Water was added so that distillation started at 110° C.,

and distillation was continued until 75–100 cc. of distillate was collected. Water was added through the funnel so that the temperature rose no higher than 135° C. By this method practically all interfering ions were separated. The distillate was made alkaline to phenolphthalein, concentrated to 20 cc., transferred to a 250 cc. Erlenmeyer flask along with 20 cc. of 95% ethyl alcohol and six drops of indicator, which is a 0.5% solution of sodium alizarin-sulphonate. Armstrong used only three drops but the writers obtained better results with the larger quantity. The contents of the flask was decolorized with 0.2 *N* hydrochloric acid, one drop being added in excess. This was then titrated to a faint permanent pink with standard thorium nitrate solution from a 10 cc. microburette. After subtracting the blank required for the formation of the thorium lake, which amounted to 0.03 cc., the parts per million of fluorine in the water were calculated. The thorium nitrate solution, the concentration of which was between 0.01 *N* and 0.02 *N*, was standardized against a 0.02 *N* solution of sodium fluoride. There is a remarkable similarity between this modified method and the method reported in Armstrong's most recent paper (2).

The colorimetric methods are more convenient than the titration method as more samples can be run at one time and smaller amounts of water are required. The titration method, however, can be used for colored waters where the colorimetric method is unsatisfactory owing to the masking of the end point, and for waters where such interfering substances as sulphate or phosphate ions are present in large quantities.

Information on mottled enamel so far collected in the province indicates that there are several districts in which the tooth defect is fairly widespread. As a general rule the attack on the teeth is slight, the mottling consisting of white opaque spots on the upper teeth, although several cases have been observed in which yellow patches were noticed.

Fig. 1 is a map of the southern half of the province of Alberta. There are apparently two areas in the province where mottled enamel of the teeth has been observed, one in the vicinity of Lethbridge and the other in the vicinity of Red Deer. The malady is not endemic in all districts of each of these areas, but it would seem that some districts are free from this tooth defect.

In the Lethbridge area the mottling is most prevalent in and around Claresholm (B) and Granum (C). (Letters refer to Fig. 1.) The water supply comes from deep wells, and in those which have been examined fluorine content is high. Unaffected children in these districts obtained their drinking water from other wells which are shallow and contain less than 1 p.p.m. of fluorine. A mild type of mottled enamel is found at Cardston (F) and in its vicinity. In this district mottling of the teeth of animals has been observed. The water supply in this district consists of creeks, sloughs, and deep wells. Those who use creek water in the town exhibit mottling, but samples of water from this source taken in the winter and early spring show low fluorine content. It may be that the creek obtains part of its supply in the summer from mountain springs which do not flow in the winter, and

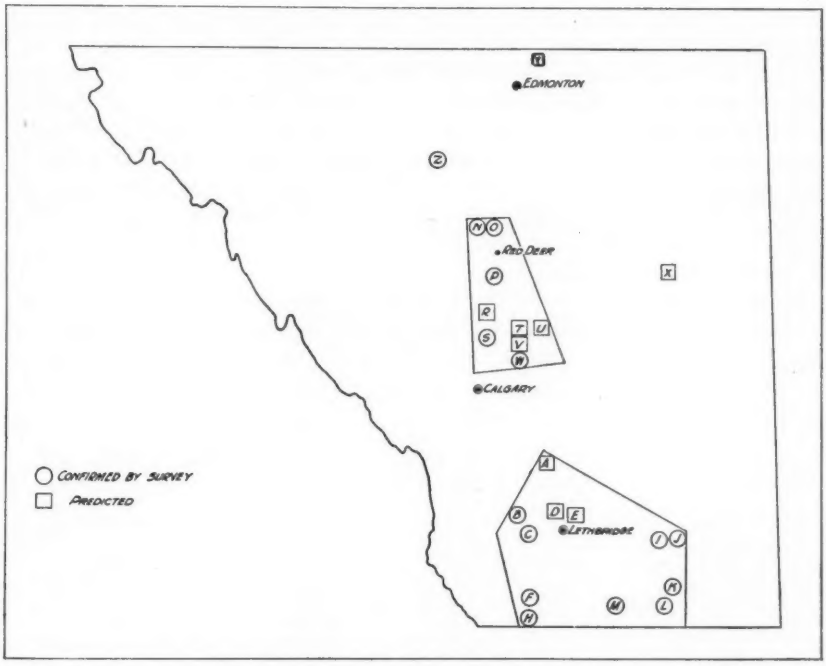


FIG. 1. *Areas in Alberta in which mottled enamel of the teeth has been observed.*

thus the water varies in fluorine content. Arrangements were made to obtain monthly samples during the summer, but the samples were lost or the bottles were broken in the mail. Mottling of the teeth also occurs 15 miles south at Kimball (H). A number of cases have been reported from Foremost (K), Grassy Lake (I), Burdett (J), and Lucky Strike (L). Water was received from all these points. Confirmation of the relation between mottled enamel and high fluorine content was obtained from the first three points. Affected people use water from deep wells. However, the water from a deep well at Lucky Strike is quite low in fluorine. Most of the cases in this district are users of water from shallow wells from which samples have not yet been obtained. Undoubtedly, as more information is received, the affected part of this area will be increased. One case has been reported from Milk River (M), but no water from this place has been examined. From the fluorine content of waters from other points it is predicted that cases of mottling will be found at Vulcan (A), Barons (D), and Picture Butte (E).

Reports on the Red Deer area are not so numerous as in the more southern area. Clinical evidence of cases from Innisfail (P), Didsbury (S), Beiseker (W) Bentley (N), and Blackfalds (O) have been obtained, and a relation was found to exist between mottled enamel and high fluorine content. It is expected that cases of mottled enamel will be found at Three Hills (U), Olds (R),

Acme (V), and Allingham (T). The deep wells in this area are mostly high in fluorine content, while the shallow wells are low in fluorine.

Mottled enamel also occurs west of Wetaskiwin (Z), but at the present time nothing is known of the character of water used in the district. Information just obtained indicates a number of mild cases near Tawatinaw (Y). Single cases of mottling have been reported from Calgary, Wabamum, and Fawcett, but the water supplies from all three were low in fluorine. A number of other parts of the province may be affected but such information is not available. From water analyses it is expected that there will be some cases near Coronation (X) and Viking.

In this water survey 254 samples have been analyzed. The fluorine contents are shown in Table I. Depths of wells are given. For convenience, the province has been divided into five parts; *(a)* the Peace River area,

TABLE I

Sample No.	Place	Depth of well, ft.	Fluorine, p.p.m.	Sample No.	Place	Depth of well, ft.	Fluorine, p.p.m.
(a) Peace River Area							
31	Bad Heart	—	0.0	109	Peace River	28	0.85
87	Chinook Valley	12	0.5	42	Valhalla Centre	37	0.1
217	Grimshaw	42	0.4	43	Valhalla Centre	110	0.5
18	Peace River	—	0.1	106	Wanham	8	0.4
71	Peace River	48	0.2	91	Whitelaw	40	1.1
(b) Central Alberta Area							
60	Alcomdale	22	0.2	58	Edson	—	0.0
54	Alliance	—	0.35	211	Elbridge	22	0.4
103	Andrew	35	0.3	159	Elk Island Park	—	0.75
104	Andrew	30	0.3	150	Elk Point	15	0.5
120	Andrew	30	0.3	59	Evansburg	—	0.05
251	Ardrossan	148	0.15	28	Fawcett	—	0.25
77	Athabasca	24	0.2	137	Fawcett	15	0.3
240	Berrymoor	50	0.05	189	Gratz	42	0.2
116	Beverly	—	0.2	84	Hairy Hill	60	0.1
250	Blackfoot	208	0.3	145	Hardisty	—	0.1
158	Botha	35	0.5	30	Hayter	—	0.2
152	Busby	31	0.8	238	Heath	50	0.05
221	Carvel	—	1.1	202	Heath	410	0.4
209	Cousins	Slough	0.7	220	Heath	40	0.35
252	Cherhill	26	0.3	160	Hobbema	250	1.1
204	Clandonald	—	0.4	117	Holden	8	0.1
176	Cold Lake	60	0.3	231	Inland	225	0.35
142	Condor	—	0.1	83	Hughenden	238	0.25
99	Cooking Lake	25	0.3	230	Innisfree	68	0.15
181	Cooking Lake	—	0.2	213	Jasper	Lake	0.05
143	Daysland	—	0.3	244	Kingman	144	0.25
232	Derwent	65	0.35	12	Kitscoty	42	0.6
180	Dewberry	70	0.7	92	Kitscoty	30	0.3
194	Dewberry	300	0.4	124	Kitscoty	28	0.4
49	Donalda	Spring	0.6	107	Lacombe	110	0.05
		10′		88	Legal	61	0.0
183	Duhamel	84	0.1	203	Legal	325	1.3
121	Edgerton	35	0.1	212	Legoff	18	0.5
37	Edmonton	40	0.1	23	Lloydminster	140	0.1
226	Edmonton	River	0.05	144	Lougheed	—	0.5

TABLE I—*Continued*

Sample No.	Place	Depth of well, ft.	Fluorine, p.p.m.	Sample No.	Place	Depth of well, ft.	Fluorine, p.p.m.
(b) Central Alberta Area—concluded							
125	Mannville	—	0.05	3	Stettler	—	0.5
234	Marwayne	59	0.0	12	Stettler	250	0.9
7	Millet	80	0.6	61	Stettler	30	1.1
237	Mirror	175	0.6	113	South Cooking Lake	54	0.5
151	Myrnam	38	0.75	246	Springfield	8	0.35
178	Myrnam	40	0.1	24	Stony Plain	—	0.4
179	Myrnam	50	0.05	161	Tawatinaw	Stream	0.4
229	Nevis	90	0.5	119	Thorsby	—	0.6
218	Nisku	220	1.2	25	Tofield	—	0.2
140	Nordegg	River	0.2	192	Tofield	—	0.6
235	North Bank	—	0.3	130	Vegreville	22	0.3
79	Pibroch	104	0.0	4	Vermilion	140	0.1
164	Plamonden	20	0.7	68	Vermilion	125	0.05
105	Radway	—	0.0	9	Viking	206	1.0
233	Ranfurly	60	0.3	10	Viking	90	1.2
118	Rivercourse	23	0.3	50	Villeneuve	52	0.05
82	Rochfort Bridge	—	0.25	96	Wabamun	—	0.25
208	Ryley	293	0.5	165	Wainwright	—	0.25
51	Sedgwick	125	0.05	5	Westlock	125	0.8
157	Slave Lake	14	0.2	6	Westlock	Spring	0.5
1	Smoky Lake	—	0.2	219	Willingdon	38	0.8
57	Smoky Lake	—	0.3	207	Winterburn	32	0.35
2	Stettler	70	0.5				
(c) Red Deer Area (Endemic)							
98	Allingham	167	1.0	102	Olds	26	0.25
35	Acme	125	0.5	155	Olds	241	2.3
36	Acme	157	2.2	163	Olds	32	2.0
78	Bentley	60	3.0	205	Olds	157	0.3
170	Bentley	95	0.5	187	Penhold	90	0.4
171	Bentley	90	1.0	76	Red Deer	River	0.1
172	Bentley	108	0.5	182	Red Deer	40	0.1
11	Didsbury	180	1.3	248	Sunny Slope	80	0.15
154	Didsbury	45	0.7	26	Swalwell	—	0.5
199	Grainger	242	0.4	85	Three Hills	374	2.3
253	Innisfail	—	0.6	173	Three Hills	380	2.3
133	Innisfail	156	2.9	174	Three Hills	265	1.5
254	Innisfail	—	0.2	175	Three Hills	30	0.4
184	Innisfail	130	0.3	201	Three Hills	500	3.1
216	Kathryn	205	1.3				
(d) Southern Alberta Area							
32	Ardenode	—	0.4	97	Calgary	150	0.25
249	Arrowwood	74	0.3	200	Calgary	25	0.25
69	Baintree	111	0.2	67	Carbon	171	0.1
64	Banff	Cave and basin	0.9	162	Carbon	8	0.3
				80	Cochrane	45	0.0
65	Banff	River	0.1	215	Consort	187	1.2
197	Beynon	26	1.0	34	Coronation	100	1.3
223	Beynon	24	1.0	135	Coronation	180	0.5
132	Big Valley	42	0.6	136	Coronation	247	0.7
112	Blairmore	River	0.05	56	Delburne	—	0.05
33	Bottrell	—	0.1	153	Delburne	30	0.3
241	Byemoor	135	0.05	52	Drumheller	60	0.0
21	Calgary	River	0.3	110	Drumheller	River	0.1
46	Calgary	River	0.3	39	Elkton	40	0.0
62	Calgary	90	0.05	40	Elkton	60	0.2

TABLE I—*Concluded*

Sample No.	Place	Depth of well. ft.	Fluorine, p.p.m.	Sample No.	Place	Depth of well. ft	Fluorine, p.p.m.
(d) Southern Alberta Area—concluded							
222	Ensign	75	0.6	188	Okotoks	14	0.1
177	Gleichen	—	1.0	90	Pincher Creek	11	1.0
236	Ghost Pine Creek	200	1.2	128	Redcliffe	30	0.0
47	Hanna	140	0.5	13	Shepard	30	1.4
131	Hanna	114	0.03	243	Stanmore	200	0.6
129	Hartell	22	0.7	206	Strathmore	75	0.2
225	High River	150	1.4	149	Throne	180	1.4
214	Hill Spring	Spring	0.8	44	Trochu	125	0.25
239	Hubalta	280	1.7	66	Trochu	110	0.3
55	Irvine	—	0.6	70	Turner Valley	Creek	0.2
191	Lundbreck	18	0.2	210	Turner Valley	Creek	0.3
245	Manyberries	640	>1.0	100	Walsh	Spring	0.1
41	Medicine Hat	River	0.2	95	Wayne	14	0.2
198	Milo	30	0.6	190	West Wingham	40	0.1
247	Milo	185	0.5	8	Whitla	20	0.8
29	Okotoks	—	0.15	123	Winnifred	780	0.5
127	Okotoks	Creek	0.5	45	Youngstown	17	0.4
(e) Lethbridge Area (Endemic)							
108	Barons	8	0.7	169	Granum	62	3.0
156	Barons	10	1.1	185	Granum	80	2.4
227	Barons	90	0.7	186	Granum	80	0.6
48	Burdett	630	2.7	166	Grassy Lake	450	3.0
138	Burdett	40	0.4	141	Kimball	190	2.2
139	Burdett	600	1.1	134	Lucky Strike	1383	0.3
15	Cardston	Creek	0.0	89	Macleod	23	0.1
16	Cardston	124	0.1	93	Macleod	24	0.1
114	Cardston	Creek	0.1	94	Macleod	24	0.1
195	Cardston	Creek	0.25	224	Monarch	—	0.6
196	Cardston	80	0.1	193	New Dayton	6	1.2
242	Cardston	40	0.35	81	Picture Butte	Spring	1.0
19	Claresholm	98	4.15	101	Picture Butte	Spring	0.0
20	Claresholm	130	3.85	147	Picture Butte	Reser-voir	0.5
53	Claresholm	128	4.6				
122	Claresholm	—	0.5	148	Picture Butte	—	1.4
146	Coutts	400	0.7	115	Purple Springs	15	0.7
167	Coutts	115	0.9	27	Raymond	145	1.2
73	Foremost	640	1.4	74	Raymond	42	0.1
63	Granum	90	2.45	86	Taber	Spring	0.5
111	Granum	28	0	75	Vulcan	220	2.6
126	Granum	106	2.2	228	Vulcan	80	1.4
168	Granum	120	2.0				

(b) Central area, *(c)* the Red Deer endemic area, *(d)* the Southern area, and *(e)* the Lethbridge endemic area. Fig. 2 is a map of the Province of Alberta showing the location of the wells examined, and marked according to depth and fluorine content. Deep wells are those more than 80 ft. in depth. Streams and springs are included with the shallow wells. It will be seen that many districts in the southern half of the province have contributed samples, but most of the sparsely populated sections have not been examined. It will be seen that, in general, in the endemic areas the deep wells are high in fluorine.

There are, however, a number of shallow wells in the Lethbridge area that contain more than 1 p.p.m. of fluorine. These wells are either springs or are supplied by seepage from irrigation ditches.

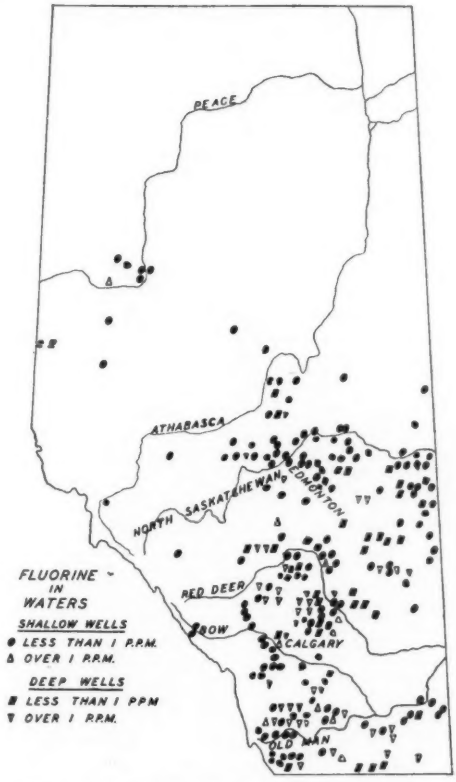
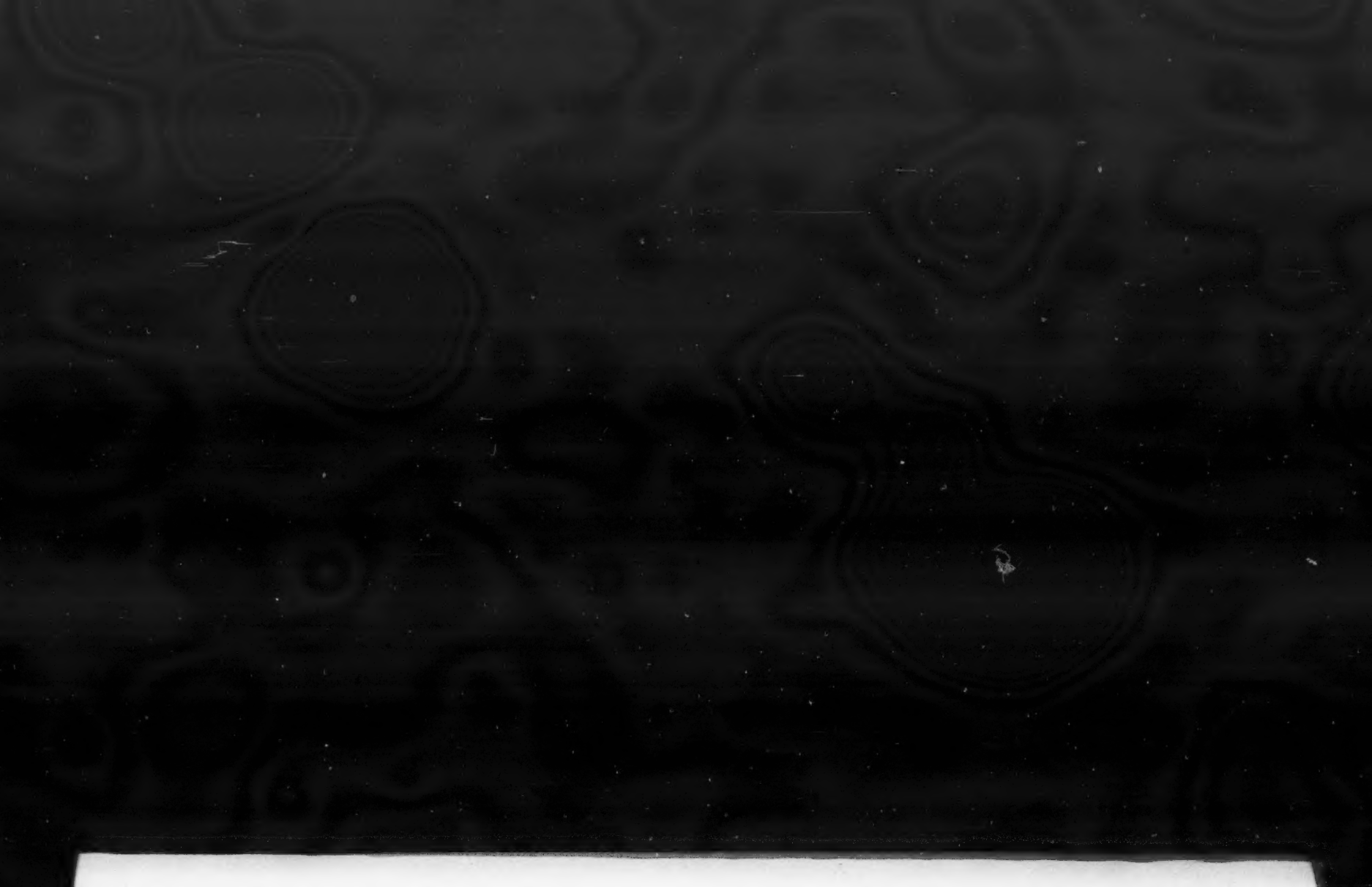


FIG. 2. *Map of Alberta showing location of the wells examined.*

No attempt has yet been made to find the source of the fluorine in the water, nor to locate the geological strata through which the waters pass.

Acknowledgments

The writers wish to acknowledge the co-operation given to them by the Provincial Department of Health, the Provincial Laboratory, the Dental Department of the University, those who collected samples of water, and those who furnished clinical evidence of mottled enamel. They also wish to thank Mr. J. S. Charlesworth who determined the fluorine content in water samples Nos. 216 to 254. This research was made possible by a grant from the Carnegie Corporation Grant Committee of the University of Alberta.

References

1. ARMSTRONG, W. D. J. Am. Chem. Soc. 55 : 1741. 1933.
2. ARMSTRONG, W. D. Ind. Eng. Chem. Anal. Ed. 8 : 384. 1936.
3. BLACK, G. V. Dental Cosmos, 58 : 129-156. 1916.
4. BORUFF, C. S. and ABBOTT, G. B. Ind. Eng. Chem., Anal. Ed. 5 : 236–238. 1933.
5. CASARES, J. and CASARES, R. Anales soc. espan. fis. guim. 28 : 1159-1162. 1930.
6. CHURCHILL, H. V. Ind. Eng. Chem. 23 : 996-998. 1931.
7. DEAN, H. T. Pub. Health Rep. 48 : No. 17, 703-734. 1933.
8. DE BOER, J. H. Chem. Weekblad. 21 : 404. 1924.
9. DE EDS, F. Medicine, 12 : 1-60. 1933.
10. FOSTER, M. D. J. Am. Chem. Soc. 54 : 4464-4465. 1932.
11. FOSTER, M. D. Ind. Eng. Chem., Anal. Ed. 5 : 234-236. 1933.
12. GREEF, A. Ber. 46 : 2511-2513. 1913.
13. KOLTHOFF, I. M. and STAINSBY, M. E. Ind. Eng. Chem., Anal. Ed. 6 : 118-121. 1934.
14. MCCOLLUM, E. V., SIMONDS, N., BECKER, R. and BUNTING, R. W. J. Biol. Chem. 63 : 553-562. 1925.
15. MCKAY, F. S. Dental Cosmos, 58 : 477-484. 1916.
16. MCKAY, F. S. Dental Cosmos, 58 : 627-644. 1916.
17. MCKAY, F. S. Dental Cosmos, 58 : 781-792. 1916.
18. MCKAY, F. S. Dental Cosmos, 58 : 894-904. 1916.
19. SANCHIS, J. M. Ind. Eng. Chem., Anal. Ed. 6 : 134-135. 1934.
20. SMITH, H. V. Ind. Eng. Chem., Anal. Ed. 7 : 23-25. 1935.
21. SMITH, M. C., LANTZ, E. M. and SMITH, H. V. Science, 74 : 244. 1931.
22. SMITH, M. C., LANTZ, E. M. and SMITH, H. V. Arizona Agr. Expt. Sta., Tech. Bull. 32 : 254-282. 1931.
23. SMITH, N. K. Chem. Trade J. 71 : 325. 1922.
24. WILLARD, H. H. and WINTER, O. B. Ind. Eng. Chem., Anal. Ed. 5 : 7-10. 1933.